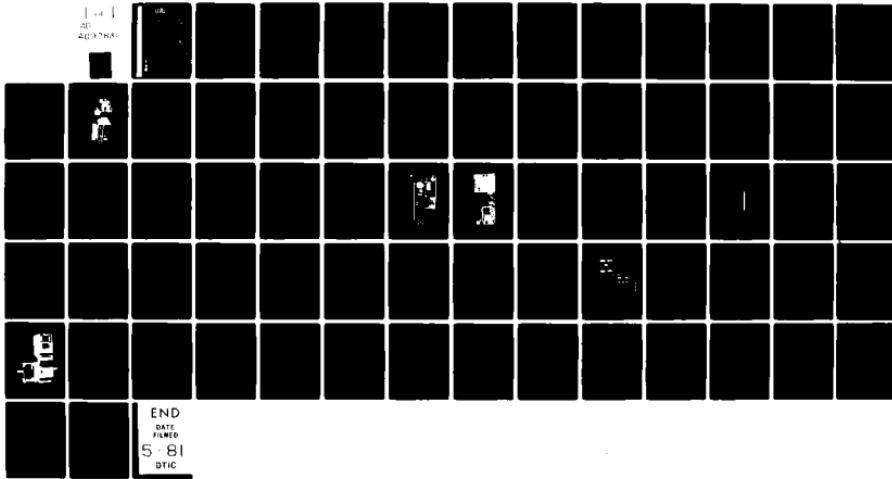


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EVALUATION OF BREADBOARD ELECTROCHEMICAL TOC/COD ANALYZER: ADVA--ETC(U)
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EVALUATION OF BREADBOARD ELECTROCHEMICAL TOC/COD ANALYZER: ADVANCED TECHNOLOGY DEVELOPMENT (U)

ANNUAL REPORT

AD A 097 831

by

J. B. Lantz, R. J. Davenport and R. A. Wynveen

August, 1980

Supported by
**US Army Medical Research
and Development Command
Ft. Detrick, Frederick, MD 21701**

Contract DAMD17-76-C-6077

Life Systems, Inc.
Cleveland, OH 44122

Project Officer: Steve Hoke, Ph.D.
Environmental Protection Research Division
US Army Medical Bioengineering
Research and Development Laboratory
Ft. Detrick, Frederick, MD 21701

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EVALUATION OF BREADBOARD ELECTROCHEMICAL TOC/COD
ANALYZER: ADVANCED TECHNOLOGY DEVELOPMENT

9 ANNUAL REPORT 31 Oct 78-15 Aug 80
by

(10) J. B. / Lantz, R. J. / Davenport and
R. A. / Wynveen

(11) Aug 1980

Prepared Under Contract DAMD17-76-C-6077

by

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(16) 3E162728A835

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
		AD-A097 831
4. TITLE (and Subtitle) Evaluation of Breadboard Electrochemical TOC/COD Analyzer: Advanced Technology	5. TYPE OF REPORT & PERIOD COVERED Annual Report, October 31, 1978 to August 15, 1980	
	6. PERFORMING ORG. REPORT NUMBER LSI TR-310-4-3 ✓	
7. AUTHOR(s) J. B. Lantz, R. J. Davenport and R. A. Wynveen	8. CONTRACT OR GRANT NUMBER(s) DAMD17-76-C-6077 ✓	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Life Systems, Inc. 24755 Highpoint Road Cleveland, OH 44122	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62720A.3E162720A835.00.078	
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Medical R&D Command Ft. Detrick, Frederick, MD 21701	12. REPORT DATE August, 1980	
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) U.S. Army Medical Bioengineering Research and Development Laboratory Ft. Detrick, Frederick, MD 21701	13. NUMBER OF PAGES 70	
	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Breadboard, Carbon Dioxide, Chemical Oxygen Demand, Dissolved Organic Carbon, Electrode, Monitor, Organic Solutes, Persulfate, Sensors, Total Carbon, Total Organic Carbon		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Advanced Breadboard TOC/COD Analyzer has been designed, fabricated, assembled and the testing program for its evaluation has been initiated. The Analyzer has been designed for simple, automated operation. It incorporates many advanced features that are designed to either provide more data than is available using other analyzers, or to more effectively integrate the Analyzer into process monitoring/control applications and applications involving water quality monitoring in remote areas. —		

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Future activities will include completion of the testing program. Also, a method of preventing interferences in the organic solute measurements due to chloride in the water samples will be developed and integrated into the Advanced Breadboard.

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EXECUTIVE SUMMARY

The Electrochemical Total Organic Carbon and Chemical Oxygen Demand Analyzers were conceptually designed for a feasibility evaluation under Contract DAMD17-75-C-5070. The Analyzers were conceptually designed to be capable of (1) providing simple, automated operation and (2) monitoring of organic solute concentrations over the range of 0.1 to 10 mg/L total organic carbon and 0.5 to 30 mg/L chemical oxygen demand. The primary applications for which they were designed were on-line process monitoring/control and water quality monitoring in remote locations. Features were therefore incorporated into the designs to provide continuous operation and to minimize the use of expendables. In situ generation of reagents and the use of an electrolyte recycle loop to extend the lifetime of the Analyzers' electrolyte were features designed to reduce logistic demands.

An evaluation of the Total Organic Carbon and Chemical Oxygen Demand Analyzers revealed that there were many similarities in the Analyzers. It was concluded that the total organic carbon and chemical oxygen demand functions could be combined in a single Analyzer that would be capable of testing and evaluating both measurement functions. Both the total organic carbon and the chemical oxygen demand measurements are based on the ultraviolet-catalyzed oxidation of organic solutes with persulfate, a strong chemical oxidizing agent. Total organic carbon is determined by measuring the amount of carbon dioxide produced through oxidation of the organic solutes, while chemical oxygen demand is determined by measuring the amount of persulfate consumed during the oxidation.

During previous phases of this program (Contract DAMD17-76-C-6077), three components of the combined Electrochemical Total Organic Carbon/Chemical Oxygen Demand Analyzer were identified, tested and evaluated, and a laboratory breadboard version of the Analyzer was assembled and tested. Important design data were obtained from the key components evaluation, and the evaluation of the Laboratory Breadboard Analyzer verified the analytical capabilities that can be anticipated from end-item analyzers.

Based on the results of these efforts, the Advanced Breadboard Analyzer was developed. This phase of the program emphasized (1) the integration of all electrochemical, mechanical and electrical components necessary within the Analyzer and (2) the development and evaluation of special design features to make the Total Organic Carbon/Chemical Oxygen Demand Analyzer uniquely compatible with on-line, process monitoring/control applications, remote monitoring of water quality and spill detection.

This report summarizes the design, fabrication, assembly and checkout of the Advanced Breadboard Analyzer. Future program activities will involve thorough testing and evaluation of its analytical performance.

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Life Systems, Inc.

FOREWORD

The work described herein was performed by Life Systems, Inc., under U.S. Army Contract DAMD17-76-C-6077 during the period October 31, 1978 to April 30, 1980. The program was directed by Dr. R. J. Davenport. The technical effort was completed by Mr. K. A. Burke, Dr. R. J. Davenport, Mr. B. W. Ellicott, Mr. G. S. Ellis, Mr. J. O. Jessup, Mr. D. W. Johnson, Mr. G. P. Koszenski, Dr. J. B. Lantz, Mr. D. Powell, Mr. J. Powell, Mr. F. H. Schubert, Mr. L. E. Wolfe, Dr. R. A. Wynveen and Dr. P. Y. Yang. Other activities were performed by Mrs. B. A. Hallick, Ms. B. M. Jaras, Mrs. D. A. Jones, Mr. E. L. Linaburg and Mrs. J. C. Torrey.

Mr. William J. Cooper and Dr. Steve Hoke were the Contract Officer's Technical Representatives for the U.S. Army Medical Bioengineering Research and Development Laboratory, Ft. Detrick, Frederick, MD 21701 during the period of this report. Dr. Deh Bin Chan represented the Civil Engineering Laboratory at Port Hueneme, CA 93010. Maj. Gary R. McNutt and Capt. Steve Termath represented the Civil and Environmental and Engineering Development Office, Tyndall Air Force Base, FL 32401. Mr. David L. Tanenbaum represented the Chemical Systems Laboratory, Aberdeen Proving Ground, MD 21010.

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LIST OF ACRONYMS

COD	Chemical Oxygen Demand
DARS	Data Acquisition and Reduction System
DOC	Dissolved Organic Carbon
IC	Inorganic Carbon
IRAD	Internal Research and Development
POC	Particulate Organic Carbon
TC	Total Carbon
TOC	Total Organic Carbon
TSA	Test Support Accessories
UV	Ultraviolet

INTRODUCTION

Environmental and public health considerations are increasing our awareness of the importance of detecting and monitoring organic contaminants in waters and wastewaters. Many laboratory instruments have been developed to determine specific organic solutes and general indices of organic contamination. However, development of instrumentation for monitoring and control applications has lagged behind the development of laboratory instruments. This is probably due to (1) the added sophistication and development time required to reliably automate the analytical functions, (2) the time required to develop special operator interfaces to simplify control of the instrument, eliminating the need for skilled chemists or technicians, (3) the time required for the development of special electrical interfaces, required in certain applications, to permit receiving commands and transmitting status indicators from the instrument to remote operator control panels or to centralized control/monitoring instrumentation and (4) the time required to develop special features to decrease the frequency of operator maintenance to make it practical to use the instrument in remote locations or where skilled maintenance personnel are not available.

The Advanced Breadboard Total Organic Carbon (TOC)/Chemical Oxygen Demand (COD) Analyzer was designed with the goal of providing these special features listed above. The design of the Advanced Breadboard incorporates a microcomputer to automate the Analyzer's startup, calibration and shutdown procedures. This simplifies operation and reduces the skill required by the operator. Electrical interfaces are provided to output the Analyzer's status and to receive remote commands. In situ hydroxide and persulfate generation, and the use of an electrolyte recycle loop were designed to extend the period between reagents resupply activities to 30 days. Therefore, the Advanced Breadboard TOC/COD Analyzer has been designed to achieve a level of performance that heretofore has not been achieved.

Background

The concept of the TOC/COD Analyzer was originated in response to the need for a monitor of residual organics dissolved in the ozonated effluent of the Water Processing Element (WPE), developed for the Medical Unit, Self-Contained, Transportable (MUST) Army field hospital. Under Contract DAMD17-75-C-5070, the concept was refined and evaluated. Water Processing Element specifications called for monitoring effluents having only 0.1 to 10 mg/L TOC and 0.3 to 30 mg/L COD. The WPE specifications also required automated, on-line operation with minimal expendables to reduce the logistic burden of operating in remote areas. Compact size and reliable performance were required because of the mobile nature of the WPE and the labor-short nature of the application.

The concept of the TOC/COD Analyzer was derived and refined to meet these requirements. Sparging the sample to remove inorganic carbon (IC) prior to measuring TOC was rejected, for example, because it requires use of compressed gases that are a logistic burden. Carbon dioxide (CO_2) and persulfate concentration measurement techniques that consume reagents were rejected for the same reason.

As part of an Internal Research and Development (IRAD) program in support of the TOC/COD Analyzer development, Life Systems, Inc. (LSI) assembled a Continuous, Chemical TOC Analyzer to demonstrate some of the concepts selected for the TOC/COD Analyzer. An inorganic carbon stripper concept, using a gas permeable membrane to extract inorganic carbon from the sample was assembled and proven. An ultraviolet (UV) reactor was also assembled and tested, and a commercially available CO₂ sensor was adapted for measuring TOC in the Analyzer.

During the present contract (DAMD17-76-C-6077), the Analyzer concept was tested and evaluated. Key analyzer components first were assembled and individually tested,⁽²⁾ then integrated and tested as part of the Laboratory Breadboard TOC/COD Analyzer (Figures 1 and 2).⁽³⁾ The Laboratory Breadboard demonstrated that the TOC measurement, as implemented in the TOC/COD Analyzer, agreed well with known concentrations (Figure 3) and with measurements made using a commercial laboratory TOC Analyzer (Tables 1 and 2).

Uncalibrated COD values were theoretical for acetic acid (refractory) but below theoretical for some less refractory organics, due to partial UV/dissolved air oxidation. Once the Analyzer was calibrated with potassium acid phthalate (KHP), COD's for those organics approached theoretical (Figure 4). Natural water COD's were somewhat higher than obtained by the dichromate method (Tables 1 and 3), indicating that the samples were more refractory than KHP.

The Laboratory Breadboard demonstrated that the TOC/COD Analyzer could provide the performance characteristics necessary for process monitoring/control applications and remote water quality monitoring.

At this point in the development, applications other than monitoring ozonated effluents were proposed for the TOC/COD Analyzer. Some of these required measurements of samples having more than 100 mg/L TOC or 300 mg/L COD. Samples containing particulates were also considered for the first time. As a result, the design specifications of the TOC/COD Analyzer underwent changes to satisfy the needs of these new applications. The design requirements and specifications of the Advanced Breadboard TOC/COD Analyzer reflect these changes and the requirements developed during testing of the Laboratory Breadboard.

Program Objectives

The objectives of the Advanced Breadboard TOC/COD Analyzer development program were as follows:

- 1.0 To design, fabricate and assemble the Advanced Breadboard TOC/COD Analyzer.
- 2.0 To assemble and checkout required Test Support Accessories (TSA).
- 3.0 To establish, implement and maintain a Mini-Product Assurance Program.
- 4.0 To test and evaluate the design and performance of the TOC/COD Analyzer.

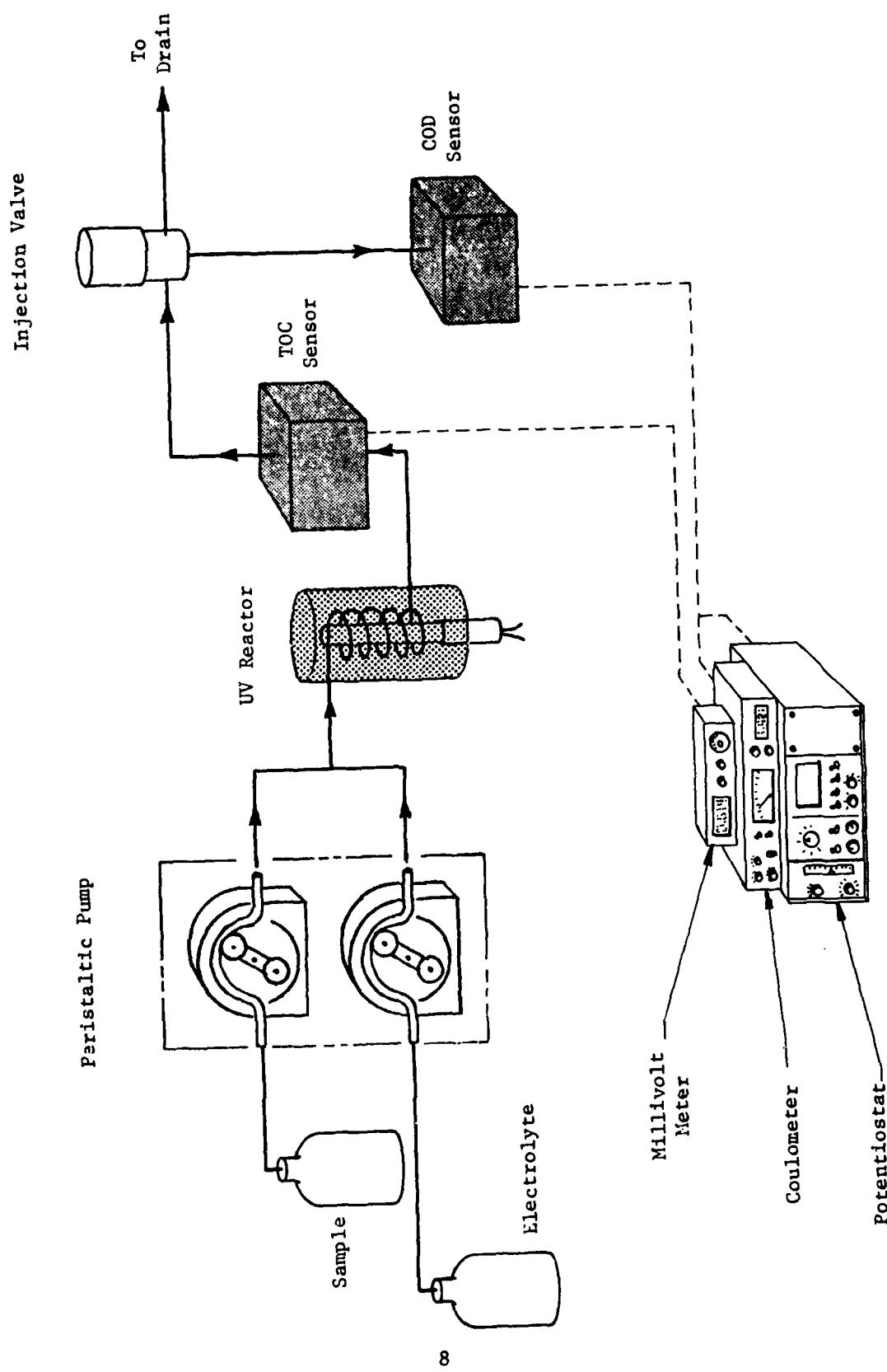


FIGURE 1 SCHEMATIC OF LABORATORY BREADBOARD TOC/COD ANALYZER

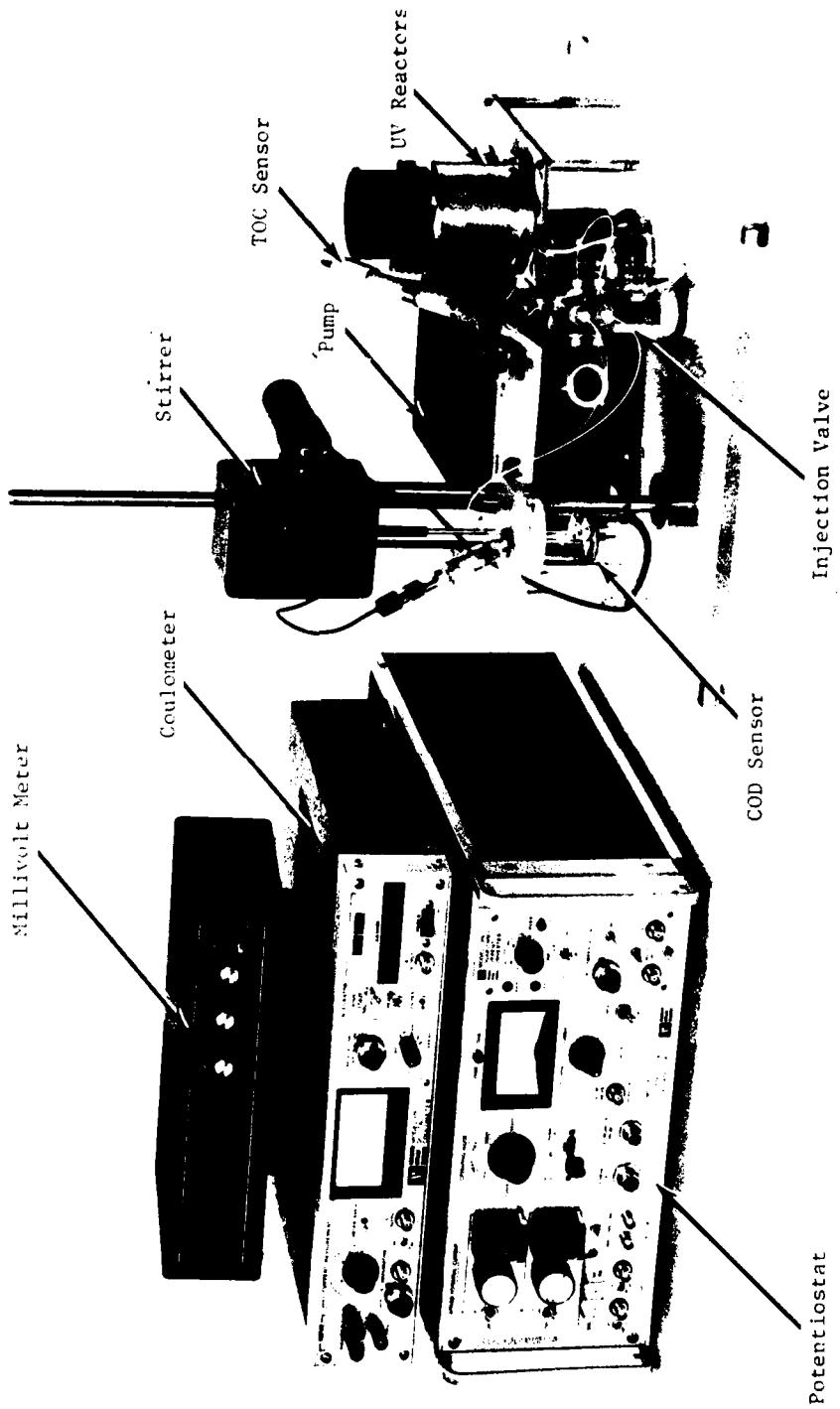


FIGURE 2 LABORATORY BREADBOARD ELECTROCHEMICAL TOC/COD ANALYZER

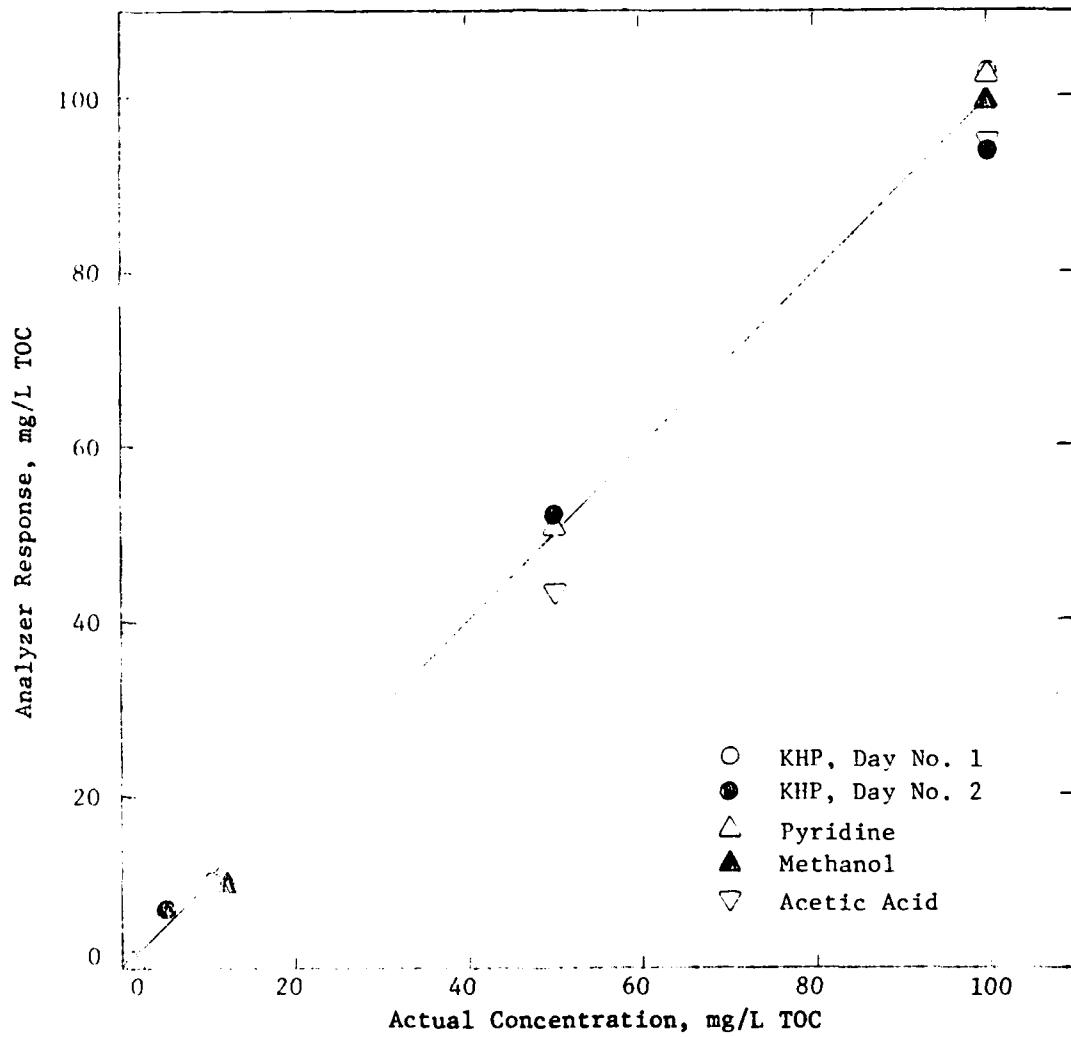


FIGURE 3 TOC RESPONSE OF LABORATORY BREADBOARD ANALYZER

TABLE 1 RESULTS OF PARTICULATE-FREE SAMPLE ANALYSES FOR LABORATORY BREADBOARD ANALYZER

Sample	<u>Cl⁻ Concentration, mg/L</u>	<u>TOC Concentration, mg/L (b)</u>			<u>COD Concentration, mg/L (b)</u>		
		<u>Analyzer Standard</u>	<u>Reported</u>	<u>Analyzer Standard</u>	<u>Reported</u>	<u>Analyzer Standard</u>	<u>Reported</u>
Demand Sample No. 1:							
1st Analysis	0	6.0	5.8	6.1	16.2	--	15.4
2nd Analysis	0	6.4	--	6.1	18.9	--	15.4
3rd Analysis	0	6.2	--	6.1	19.9	--	15.4
4th Analysis	0	6.2	--	6.1	18.3	--	15.4
Average	0	6.2	--	6.1	18.3	--	15.4
Tap Water No. 1	28	2.6	2.7	--	11.1	6.5	--
Tap Water No. 2	--	0.4	1.0	--	--	--	--
Well Water	7	3.0	3.0	--	6.4	4.1	--
Treated Sewage, Filtered	116	4.3	4.5	--	17.5	11.2	--

(a) From EPA, Cincinnati, OH

(b) Standard and reported concentrations correspond to values obtained with a standard TOC Analyzer (Dohrmann DC 50) and reported by the EPA, respectively.

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TABLE 2 RESULTS OF TOC ANALYSES OF PARTICULATE-CONTAINING
SAMPLES FOR LABORATORY BREADBOARD ANALYZER

<u>Sample</u>	<u>TOC Concentration, mg/L</u>		<u>TOC Recovery, %</u>
	<u>Analyzer</u>	<u>Standard</u>	
Chagrin River Water	5.0	4.8	104
Treated Sewage No. 1	9.8	9.8	100
Treated Sewage No. 2	9.5	9.4	101
Treated Sewage No. 3:			
1st Analysis	7.0	7.6	
2nd Analysis	8.0	--	
3rd Analysis	8.6	--	
4th Analysis	5.9	--	
Average	7.4		97
Raw Sewage	31.1	27.3	114
		Average	103

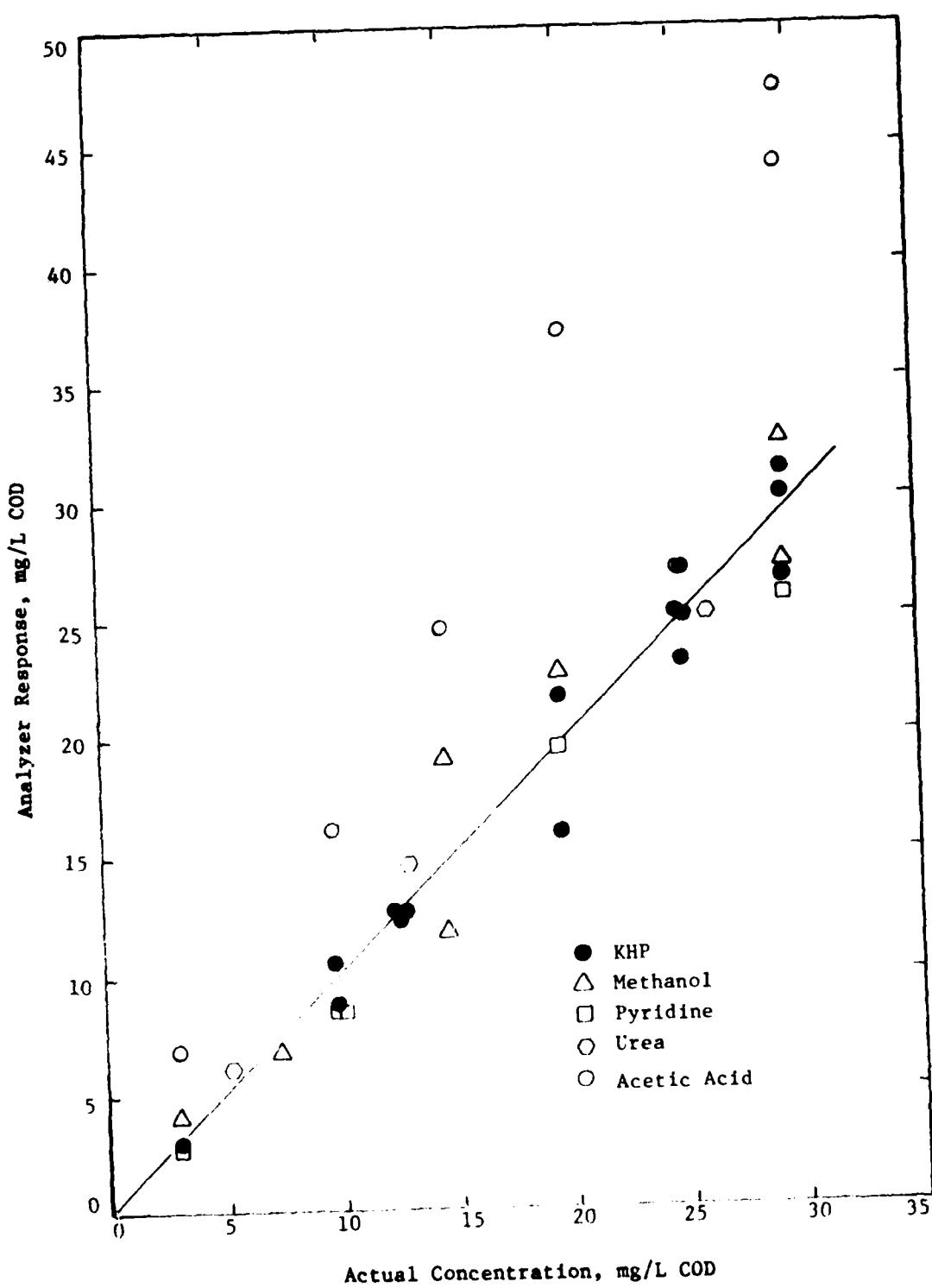


FIGURE 4 COD RESPONSE OF LABORATORY BREADBOARD ANALYZER

TABLE 3 RESULTS OF COD ANALYSES OF PARTICULATE-CONTAINING
SAMPLES FOR LABORATORY BREADBOARD ANALYZER

<u>Sample</u>	<u>COD Concentration, mg/L</u>	<u>Analyzer</u>	<u>Standard</u>	<u>Recovery, %</u>
Treated Sewage No. 1	20.4		16.8	121
Treated Sewage No. 2	30.4		23.0	132
Raw Sewage	166.8		164.5	101
		Average	118	

- 5.0 To perform supporting studies necessary to define design parameters of the Analyzer.
- 6.0 To incorporate the Contractor's data management functions to provide internal procedures for control of the collection, preparation, quality, assessment, distribution and maintenance of data.
- 7.0 To incorporate the management needed to successfully meet the program's Cost, Schedule and technical Performance requirements, to coordinate with the Contracting Officer's Technical Representative (COTR) through telephone discussions and to result in Customer satisfaction.
- 8.0 To design, fabricate, assemble and checkout the Advanced Breadboard Analyzer persulfate generation cell.
- 9.0 To evaluate advanced COD sensor concepts for ultimate incorporation in the Analyzer.

Definitions

Commonly used indices of organic solute concentrations are defined below:

1. Chemical Oxygen Demand (COD): COD represents the oxygen (O_2) equivalents consumed in the chemical oxidation of oxidizable solutes (primarily organic species). The COD in the sample is determined by measuring the quantity of a strong chemical oxidizing agent consumed during oxidation of the solutes. COD is expressed in units of mg/L.
2. Dissolved Organic Carbon (DOC): DOC values are based on the concentration of soluble carbonaceous organic solutes in the sample, and the measurement represents the concentration of carbon in the solutes. DOC is expressed in units of mg/L.
3. Inorganic Carbon (IC): IC values represent the concentration of carbon in the sample existing in the form of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and dissolved CO_2 . Inorganic Carbon is expressed in units of mg/L.
4. Total Carbon (TC): TC values equal the sum of IC and total organic carbon (TOC) concentrations. Total carbon is expressed in terms of mg/L.
5. Total Organic Carbon (TOC): TOC is the concentration of carbon in the sample, present in the form of dissolved and particulate carbonaceous compounds. Total organic carbon concentrations are expressed in units of mg/L.

DESIGN GOALS

The design goals for the Advanced Breadboard are listed in Table 4. These are based on the results of the Laboratory Breadboard and the extension of the TOC/COD Analyzer to new potential applications.

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TABLE 4 DESIGN GOALS

Self-Contained, Packaged Design

Concentration Range

0.1 - 500 mg/L TOC
100 - 1500 mg/L COD

Continuous, On-Line Sampling

Direct Concentration Readout

**Analog Outputs Compatible with Strip Chart
Recorders and DARS**

In Situ Persulfate Generation

Acceptance of up to 300 mg/L Cl⁻

Automated Calibration

- Autozero
- Autospan

Measurement of TOC, DOC and TC

**Acceptance of up to 0.3 mm diameter particles with
homogenizer accessory**

Unattended Operation for 30 Days

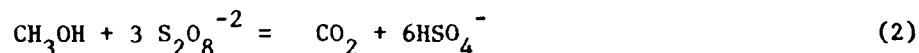
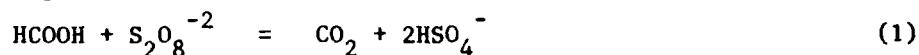
Electrolyte Recycle Loop

The extended ranges of organic concentration to be encountered in several applications are shown in Figures 5 and 6 for TOC and COD, respectively. The upper concentration goal of the Advanced Breadboard was increased to 500 mg/L TOC and 1500 mg/L COD on the basis of this data. Since COD is a difference measurement (e.g., a measurement of the oxidizing agent concentration before and after the organic oxidation), it would be impractical to attempt detecting very small decreases in the large persulfate concentration necessary to oxidize 1500 mg/l COD. Therefore, a range of 150 to 1500 mg/L was accepted as the COD concentration range for the Advanced Breadboard. Future Analyzers could incorporate provisions for multiple concentration ranges by generating smaller persulfate concentrations for measurements of less than 150 mg/L COD.

In summary, the purpose of the Advanced Breadboard was extended from monitoring only ozonated effluents to also monitoring natural waters and treated water and wastewater. Environmental specifications used for the design are presented in Table 5, and anticipated sample specifications are listed in Table 6. Table 7 lists the hardware and performance specifications used to design the Advanced Breadboard. Values used for these specifications were selected because of their projected compatibility with the above applications.

BASIS OF TOC/COD ANALYZER OPERATION

Total organic carbon is a general index of organic solute concentrations. It defines the quality of carbon in the sample that exists in the form of organic solutes. Unlike TOC, COD is a measure of the oxidation state of the organics, as well as their concentration. Organic solutes in higher oxidation states, such as formic acid (HCOOH), consume less persulfate during oxidation to CO₂ than do less highly oxidized organics. This is illustrated with HCOOH and methanol (CH₃OH) in Equations 1 and 2:



Because of this difference between TOC and COD measurements, it is possible that two samples, having equal TOC concentrations, may have significantly different COD concentrations. An operator would obtain qualitative information about the nature of the organic contaminants if he could determine the COD/TOC ratio. This is data uniquely provided by the Advanced Breadboard TOC/COD Analyzer.

The TOC/COD Analyzer incorporates six processes:

1. Electrochemical generation of the persulfate from an acidic electrolyte.
2. Continuous sampling and mixing of the sample with the electrolyte and persulfate.
3. Removal of IC (HCO₃⁻, CO₃²⁻ and dissolved CO₂) from the sample.
4. Oxidation of the organics.
5. Measurement of the CO₂ produced and persulfate consumed in the oxidation.
6. Elimination of the water introduced during sampling from the electrolyte.

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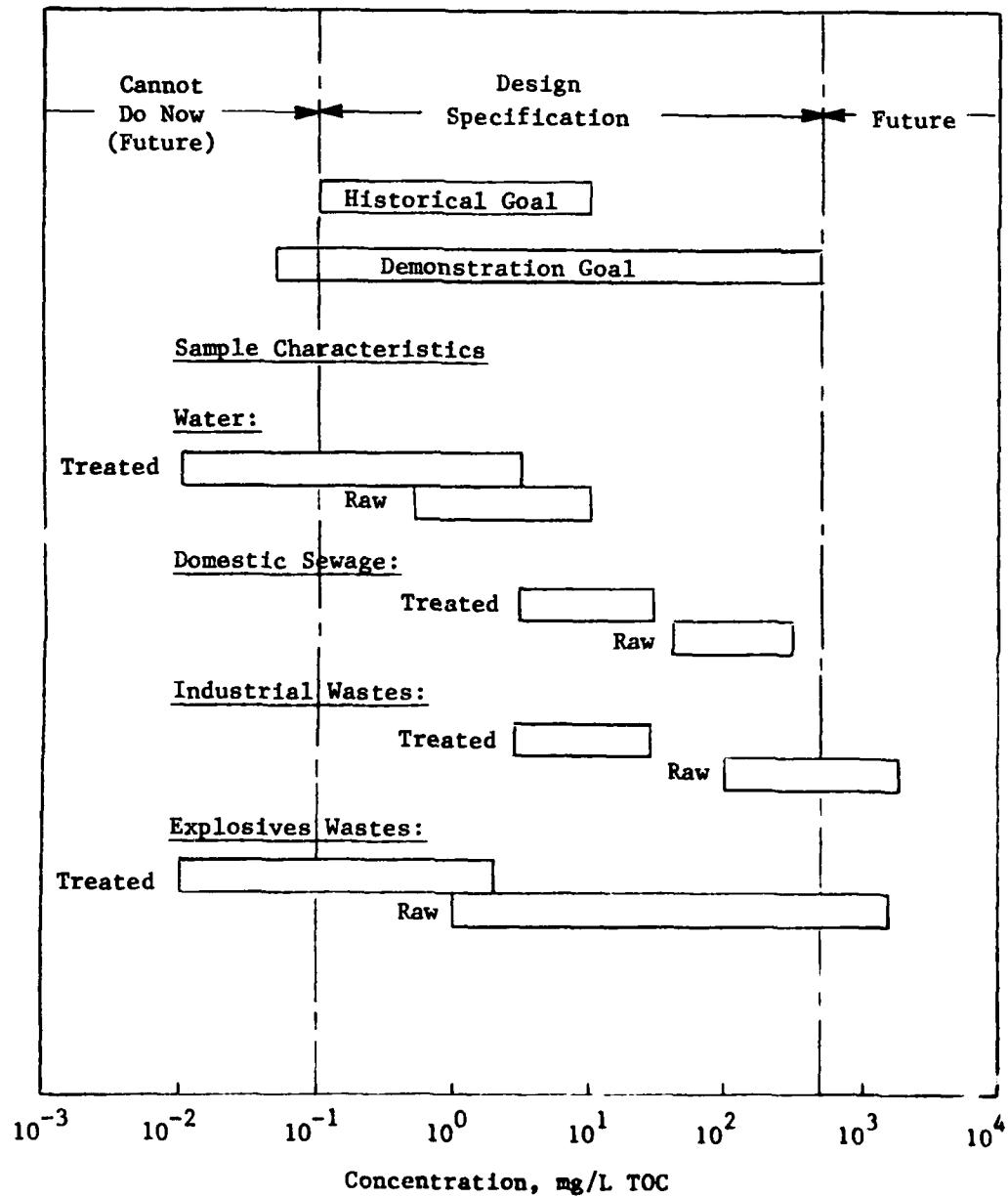


FIGURE 5 TOC DESIGN RANGE GOAL OF ADVANCED BREADBOARD
TOC/COD ANALYZER VERSUS SAMPLE TYPE

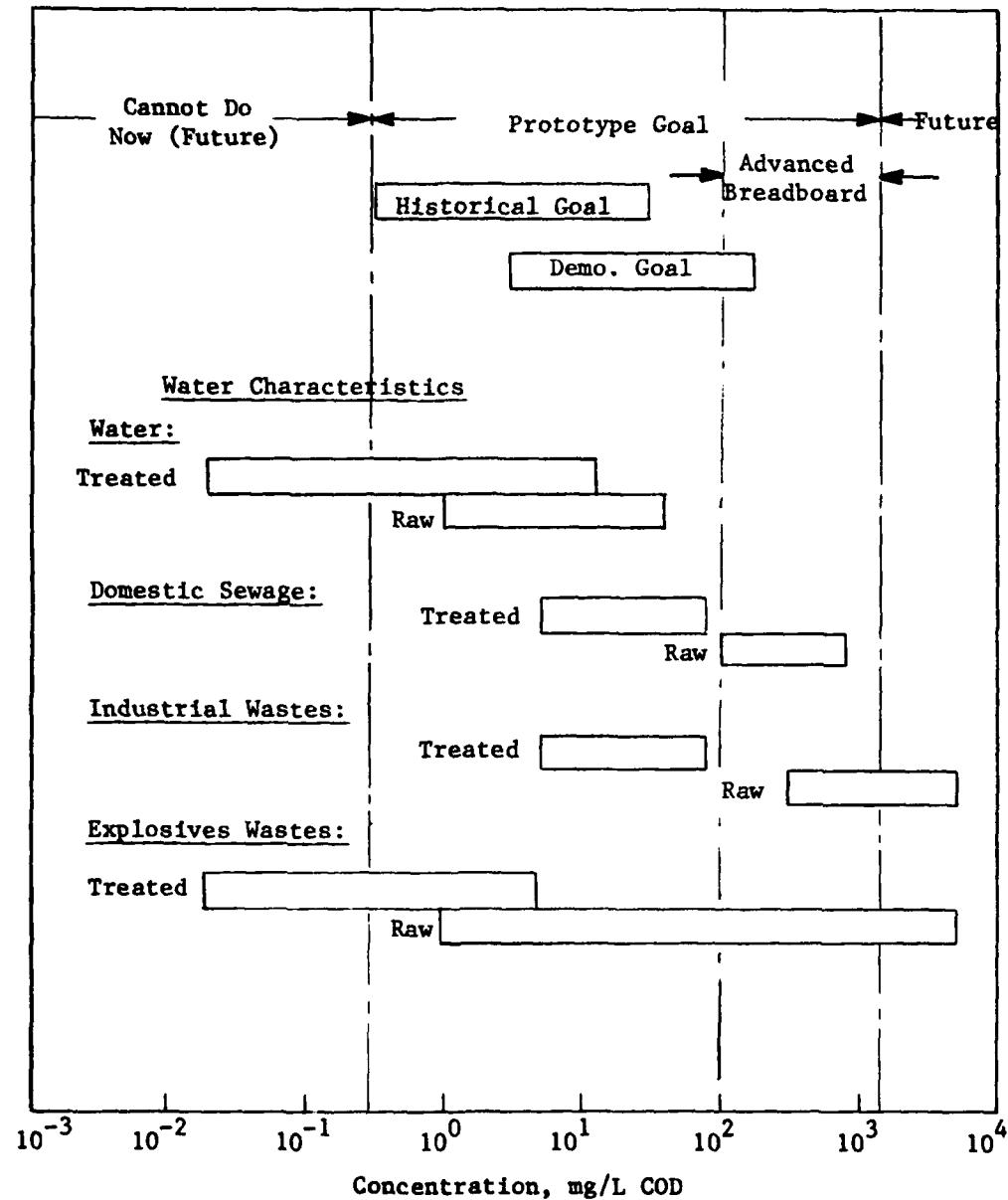


FIGURE 6 COD DESIGN RANGE GOAL OF ADVANCED BREADBOARD TOC/COD ANALYZER VERSUS WATER TYPE

TABLE 5 ENVIRONMENTAL SPECIFICATIONS FOR ADVANCED
BREADBOARD TOC/COD ANALYZER

Operating Environment	LSI Instrumentation Development Laboratory		
	1 Air Conditioned/Heated	2 Low Air Contaminant Levels	
	Range		
	Low	Nominal	High
Temperature, C	0	22	40
Pressure, mm Hg	660	760	813
Relative Humidity, %	5	50	95
Vibration, Amplitude/ Frequency, cm/Hz	0.013/5	0.013/5	0.13/33
Airborne Particulates, mg/L	0	1	5
Combustible Gases, %	0	0	1
Corrosive Gases, mg/L	0	1	2
Salt Spray, mg/L	0	0	1
Inclination, Degrees from Vertical	0	0	5

TABLE 6 SAMPLE SPECIFICATIONS (GOALS)

Water Types Assumed:

1. Raw Water
2. Treated Sewage
3. Raw Sewage

	Range		
	Low	Nominal	High
Organic Concentration, mg/L			
TOC	0.1	100	500
COD	100	300	1,500
Total Solids, mg/L	0	525	5,000
Total Dissolved Solids, (a) mg/L	0	500	5,000
Total Suspended Solids, (c) mg/L	0	20	350
Total Settleable Solids, (d) mg/L	0	5	20
Inorganic Carbon (as C), (e) mg/L	0	10	100
Bicarbonate (as HCO_3^-), mg/L	0	51	500
Carbonate (as CO_3^{2-}), mg/L	0	0	10
Silica, mg/L	1	10	30
Iron, mg/L	0	0.3	0.5
Manganese, mg/L	0	0.1	0.2
Calcium, mg/L	0	50	600
Magnesium, mg/L	0	50	600
Sodium, mg/L	0	70	1,000
Potassium, mg/L	0	3	10
Chloride, mg/L	0(f)	75	300(g)
Sulfate, mg/L	0	100	1,000
Fluoride, mg/L	0	0	10
Nitrate (as NO_3^-), mg/L	0	2	5
Ammonia (as NH_3), mg/L	0	10	50
Total Phosphorous, mg/L	0	5	20
Hardness as CaCO_3 , mg/L	0	90	800
Alkalinity as CaCO_3 , mg/L	0	50	200
pH	5.0	7.0	10.5
Conductivity, $\mu\text{mho}/\text{cm}$	0	800(h)	1,660
Temperature, C (F)	0 (32)	22 (72)	40 (104)
Pressure, Pa (psig)	-	101 (0)	-

(a) Diameters less than 10^{-6} mm

(b) Diameters greater than 10^{-6} mm

(c) Diameters greater than 10^{-2} mm

(d) Corresponds to the HCO_3^- and CO_3^{2-} concentrations cited

(e) Above 100 mg/L inorganic carbon by special design

(f) Provides for the application where no Cl^- is present, thereby allowing analyzer simplification

(g) Levels greater than 300 mg/L require special design modifications

(h) Corresponds to about 500 mg/L total dissolved solids

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TABLE 7 ADVANCED BREADBOARD ELECTROCHEMICAL TOC/COD
ANALYZER SPECIFICATIONS (GOALS)

<u>DESIGN DATA</u>		Range		
<u>Operating Conditions</u>		<u>Low</u>	<u>Nominal</u>	<u>High</u>
Sample Flow Rate, mL/min		0.58	0.60	0.62
Temperature, C (F)		0 (32)	22 (72)	40 (104)
Electrolyte Concentration, M		1.8	2.0	2.2
Hydroxide Concentration, M		0.04	0.05	0.06
Persulfate Concentration, M		0.26	0.27	0.28
Calibration Frequency, Times/d		0	1	5
Persulfate Generator Temp., C (F)		9 (48)	10 (50)	11 (52)
Liquid Discharge, mL/min		0.29	0.30	0.31
<u>Performance Characteristics</u>				
Concentration Range, mg/L				
TOC		0.1	100	500
COD		100	300	1,500
Linearity, % Full Scale				
TOC		0.4		
COD		0.3		
Detection Limits, mg/L				
TOC		0.1		
COD		100		
Accuracy, %		Concentration, mg/L		
		1.0	10	100
				1000
TOC		30	3	1.3
COD		-	-	50
Precision, Standard Deviation, mg/L				
TOC		0.3	0.3	0.5
COD		-	-	50

continued-

Table 7 - continued

	<u>Baseline Analyzer</u> ^(a)	<u>Analyzer with Added Capabilities</u> ^(b)
Response Time, min		
TOC	11	16
COD	11	16
Startup Time, min	40 (Nominal)	
<u>Physical Characteristics</u>		
Analytical Package		
Weight, kg (lb)	20 (44)	
Volume, m ³ (ft ³)	1.2 (4.3)	
Dimensions (HxWxD), cm (in)	61x66x30 (24x26x12)	
Instrumentation Package		
Weight, kg (lb)	32 (71)	
Volume, m ³ (ft ³)	0.09 (3.3)	
Dimensions (HxWxD), cm (in)	61x51x30 (24x20x12)	
<u>Material Characteristics</u>^(c)		
Nonmetallic	Teflon, Polyethylene, Polypropylene, Polysulfone, Kel-F, Carbon, Glass	
Metallic	Platinum, Hastelloy C, Titanium	
<u>Electrical Characteristics</u>		
Current, A	3.4	
Voltage, VAC	115	
Power, W	390	
<u>Sample Characteristics</u>		
Water Types	1. Raw Water 2. Treated Sewage 3. Raw Sewage	

continued-

- (a) Without POC or TC accessories.
- (b) With POC and TC accessories.
- (c) Wetted surfaces.

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Table 7 - continued

	Range					
	Low	Nominal	High			
Organic Concentration, mg/L						
TOC	0	100	500			
COD	0	300	1,500			
Inorganic Carbon, mg/L	0	10	100			
Total Dissolved Solids, mg/L	0	500	5,000			
pH	5.0	7.0	10.5			
Temperature, C (F)	0 (32)	22 (72)	40 (104)			
Pressure, kN/m ² (psig)	-	101 (0)	-			
<u>INTERFACES</u>						
<u>Mechanical</u>						
Sample Inlet	1/16 in Swagelok					
Sample Outlet	1/16 in Swagelok					
Cooling Air Inlet	6 in dia filter					
Cooling Air Outlet	4 in dia					
<u>Electrical</u>						
Line Power	Standard Plug					
Analog Outputs	Terminal Strip					
<u>Mounting</u>						
<u>ENVIRONMENT</u>						
Temperature, C (F)	0 (32)	22 (72)	40 (104)			
Pressure, mm Hg	660	760	813			
Relative Humidity, %	5	50	95			
Inclination, Degrees from Vertical	0	0	0			
<u>MAINTENANCE LEVEL AND METHOD</u>						
<u>Normal Maintenance</u>						
Daily						
Acc. ity	1. Check instrument operation					
Time Required, h	0.25					

continued-

Table 7 - continued

Monthly	
Activities	<ol style="list-style-type: none">1. Resupply electrolyte2. Resupply standard reagents3. Resupply NaOH4. Resupply TOC sensor filling solution5. Replace Filters
Time Required, h	1.5
Bimonthly	
Activities	<ol style="list-style-type: none">1. Replace pump tubing2. Replace TOC sensor membrane
Time Required, h	0.8
Annual	
Activity	<ol style="list-style-type: none">1. Replace inorganic carbon stripper membrane
Time Required, h	0.8
<u>Maintenance for Storage</u>	
When Analyzer is Unpowered	
Activity	<ol style="list-style-type: none">1. Open pump to release pressure on tubing
Time Required, h	0.8
When Analyzer Stored for One Month or More	
Activity	<ol style="list-style-type: none">1. Drain electrolyte, standards and internal filling solution reservoirs
Time Required, h	0.2

Other functions were added to the Advanced Breadboard Analyzer for operator convenience, to achieve enhanced Analyzer performance, to demonstrate the capabilities of the functions, or to evaluate their effectiveness. Among these additional features are:

1. A capability for filtering the sample through a 0.45 μm filter to determine DOC.
2. The capability of measuring TC.
3. Automated calibration.
4. A fast response accessory within the TOC sensor to achieve faster response dynamics.
5. Electronic aids for simplified operation and maintenance, and more effective integration of the Analyzer in automated water and waste-water treatment processes.

ADVANCED BREADBOARD TOC/COD ANALYZER

The Advanced Breadboard is composed of two major packages; the Analytical Package and the Instrumentation Package (Figure 7). These are shown mounted on the TOC/COD Analyzer Characterization Test Stand in Figure 8.

The configuration of the Advanced Breadboard provides maximum accessibility to the hardware. All four sides of the Analytical Package are accessible to the operator. The Instrumentation Package is accessible from the top, rear and both sides.

Analytical Package

The Analytical Package (Figures 8 and 9) contains all actuators, sensors, fluid handling components and the other mechanical and electrochemical devices in the Analyzer. The components are located on both sides of a vertical mounting panel, rather than in an enclosure, to facilitate assembly, debugging and maintenance of the Analyzer.

Mechanical Schematic

The mechanical schematic of the Analyzer is shown in Figure 10. During normal operation, the sample is continuously drawn into the Analyzer through a 10 μm filter that removes particles that might otherwise eventually restrict liquid flowing through the Analyzer. If DOC measurements are made, the sample also passes through a 0.45 μm membrane filter.

For IC removal during TOC or DOC measurements, the inorganic carbon stripper is used. The sample is divided into two streams. One is mixed with the acidic electrolyte (containing persulfate), and IC is immediately converted to CO_2 by the acid. The second sample stream passes through the hydroxide generator, which injects sodium hydroxide (NaOH) into the sample to make it basic.

When the acidic and basic sample streams flow through the inorganic carbon stripper, CO_2 diffuses from the acidic stream, through a gas permeable membrane, to the basic stream. Effective IC removal is thereby achieved. If TC measurements are made, the acidified sample stream bypasses the stripper.

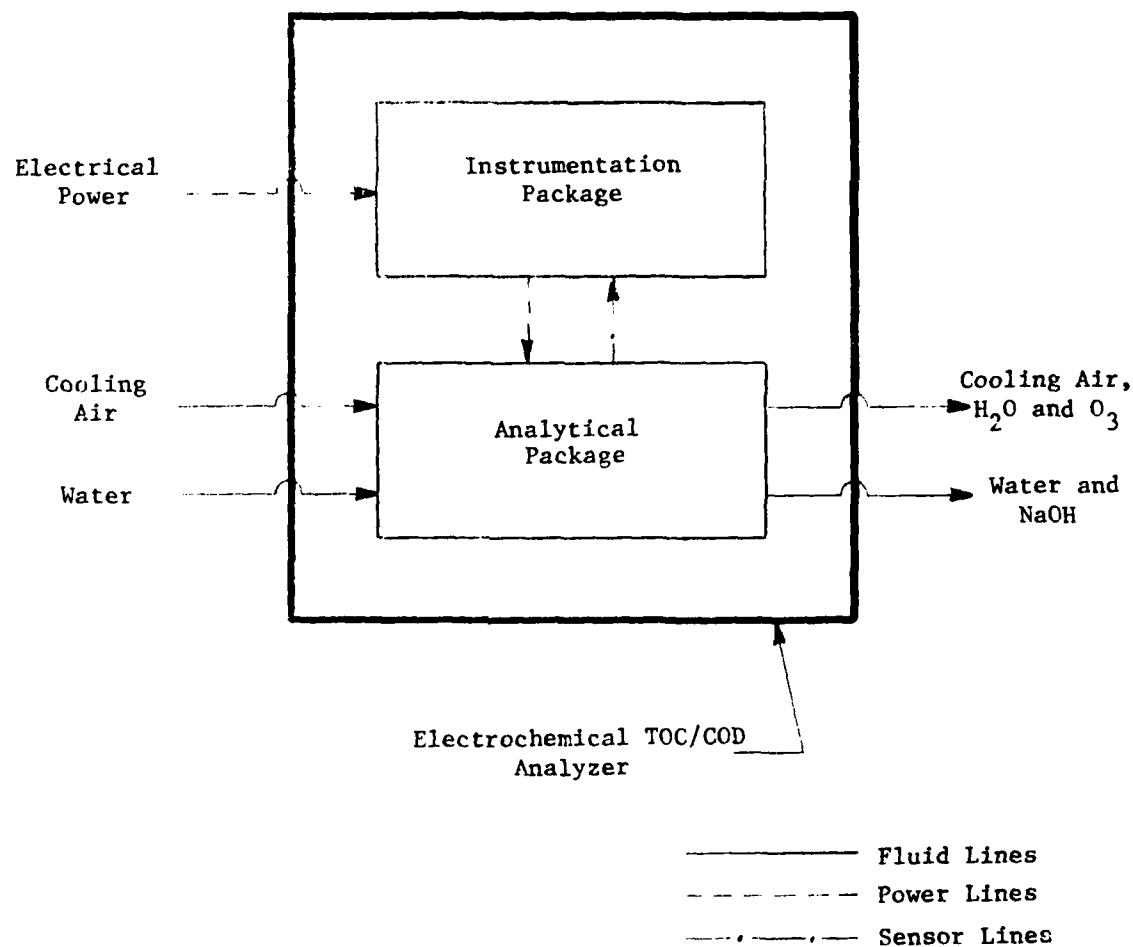


FIGURE 7 ADVANCED BREADBOARD TOC/COD ANALYZER BLOCK DIAGRAM

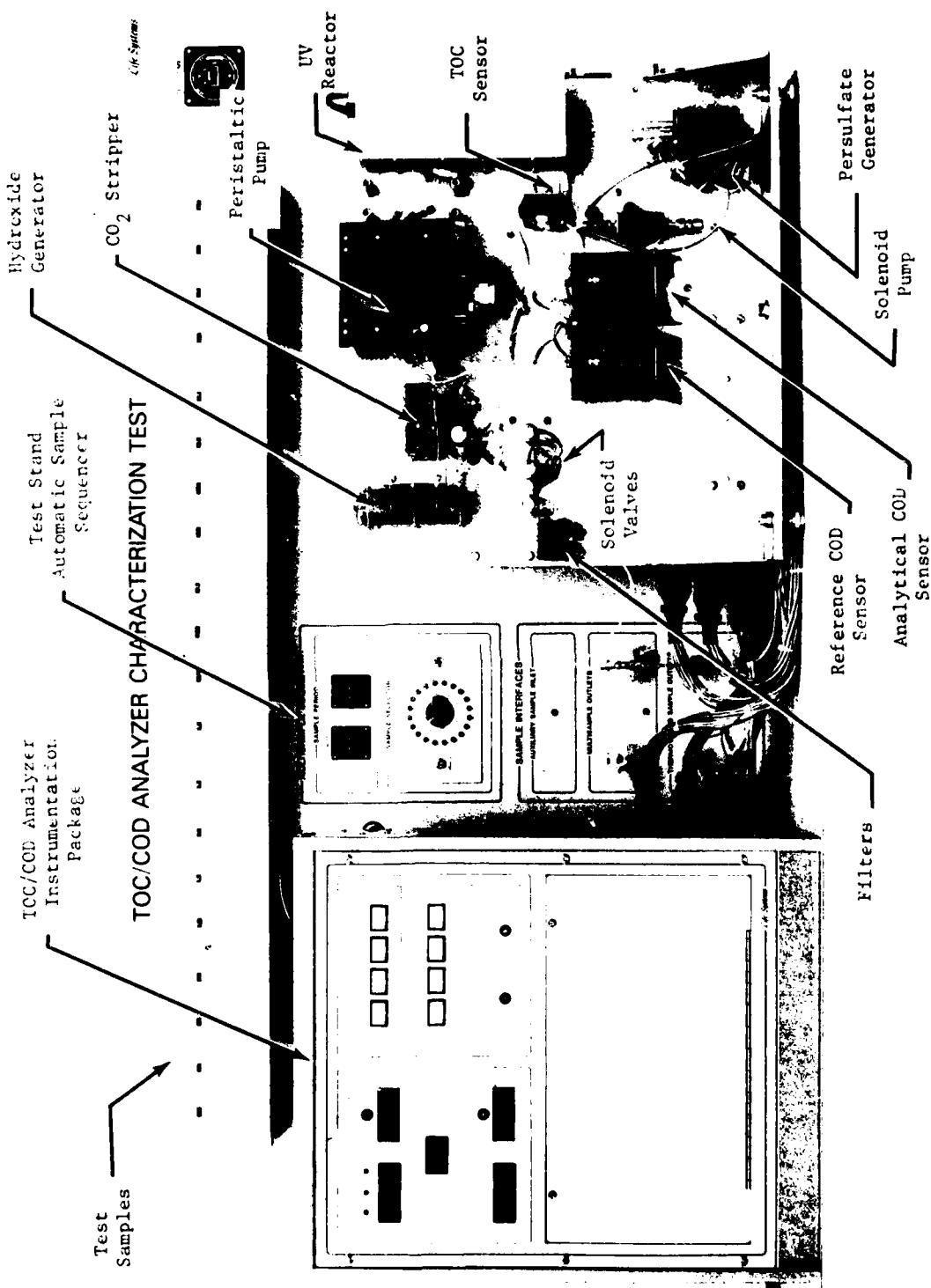


FIGURE 8 ADVANCED BREADBOARD TOC/COD ANALYZER, FRONT VIEW

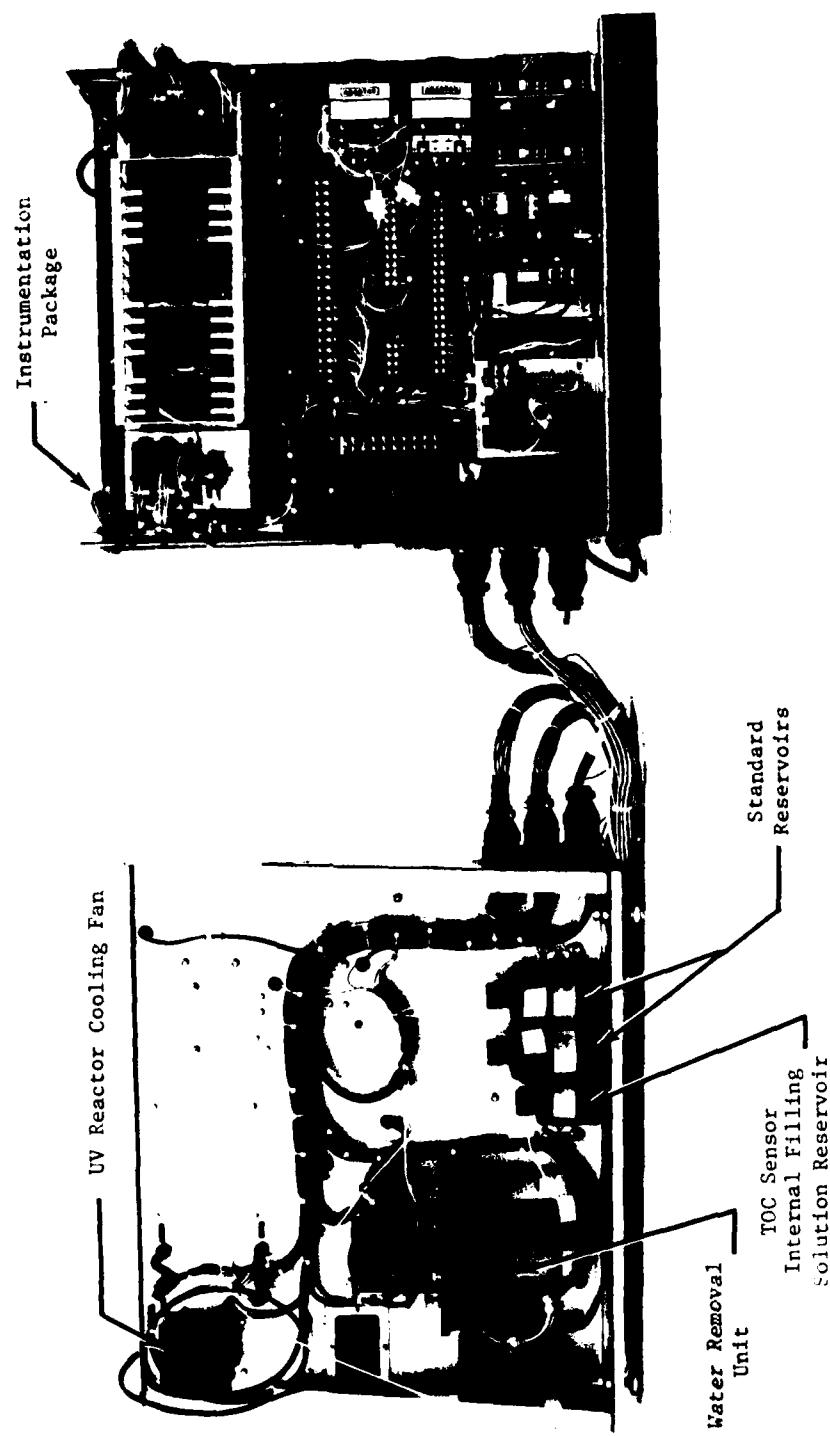


FIGURE 9 ADVANCED BREADBOARD TOC/COD ANALYZER, REAR VIEW

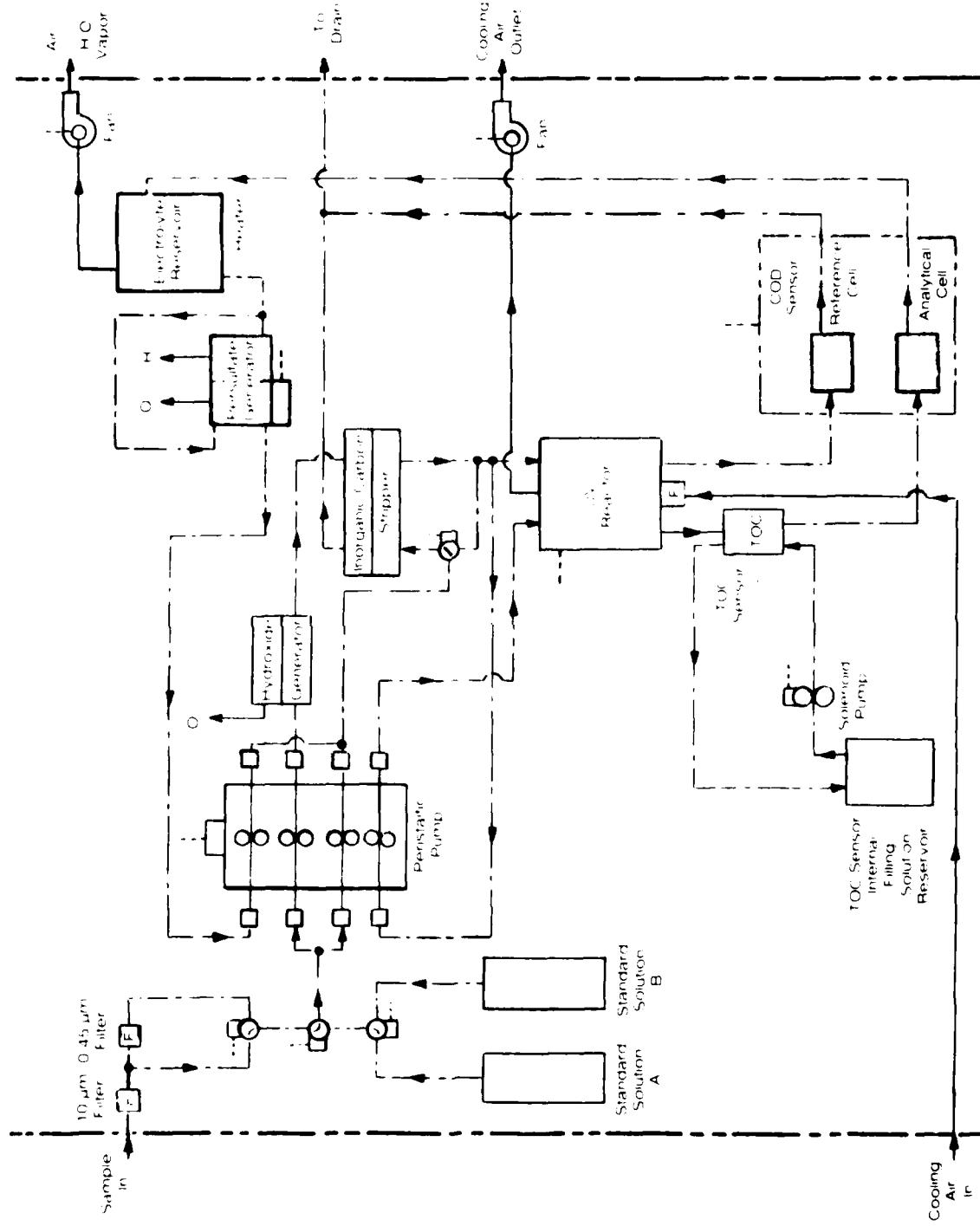


FIGURE 10 ADVANCED BREADBOARD TOC/DOC ANALYZER SCHEMATIC.

The effluent from the stripper is also divided into two streams. Both streams flow through the UV reactor, but only one flows through the quartz coil in the reactor that is exposed to UV radiation. This is called the "analytical stream." The analytical stream exits the UV reactor and flows through the TOC sensor, where CO_2 , produced by the oxidation of organic solutes (and from acidification of IC, if TC measurements are made) is measured. The analytical stream continues to the analytical cell of the COD sensor.

The COD sensor consists of two identical electrochemical cells that measure the persulfate concentration in each of the two sample/electrolyte streams. The concentration of persulfate in the analytical stream is reduced by the amount of persulfate consumed in the oxidation. However, the other stream (the "reference stream," which is not exposed to UV radiation in the UV reactor) contains the persulfate concentration that would exist if the sample contained no organics.

The difference in persulfate concentrations between the reference and analytical streams is measured by the COD sensor. The concentration difference is proportional to the COD concentration in the sample. This differential technique is designed to automatically compensate for variations in the persulfate generation efficiency in the persulfate generator, and for changes in the rate of spontaneous thermal decomposition of persulfate.

The analytical stream is returned to the electrolyte reservoir, where it is heated to remove the water added during sampling as water vapor. The electrolyte is therefore brought to its original concentration and the electrolyte is recycled to the persulfate generator. This device electrochemically oxidizes sulfate (SO_4^{2-}) in the electrolyte to generate persulfate.

The major mechanical Analyzer components are discussed in detail below.

Major Analyzer Components

Many of the features of the Advanced Breadboard Analyzer are the result of the unique or innovative components used in the Analyzer. The functional concept of each major component is summarized below.

Hydroxide Generator. The hydroxide generator, shown schematically in Figure 11, injects NaOH into a portion of the sample stream for removal of IC in the organic carbon stripper. Its operation is based on LSI's patented electrochemical valve principle. The hydroxyl ions (OH^-) are electrochemically generated in the sample stream, while sodium ions (Na^+) migrate through a cation exchange membrane from an accumulator that contains a slurry of NaOH pellets in water. The concentration of NaOH injected into the sample stream is controlled by controlling the current flowing between the electrodes in the generator.

Inorganic Carbon Stripper. The functional schematic of the stripper is shown in Figure 12. The gas-permeable membrane, through which CO_2 passes from the acidic solution to the basic solution, is shown. The IC in the sample is removed effectively because of the large CO_2 partial pressure difference that exists between the acidic solution (in which IC exists as CO_2IC) and the basic solution (in which the CO_2 is converted to the nonvolatile CO_3^{2-}).

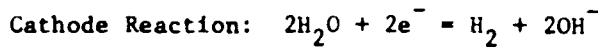
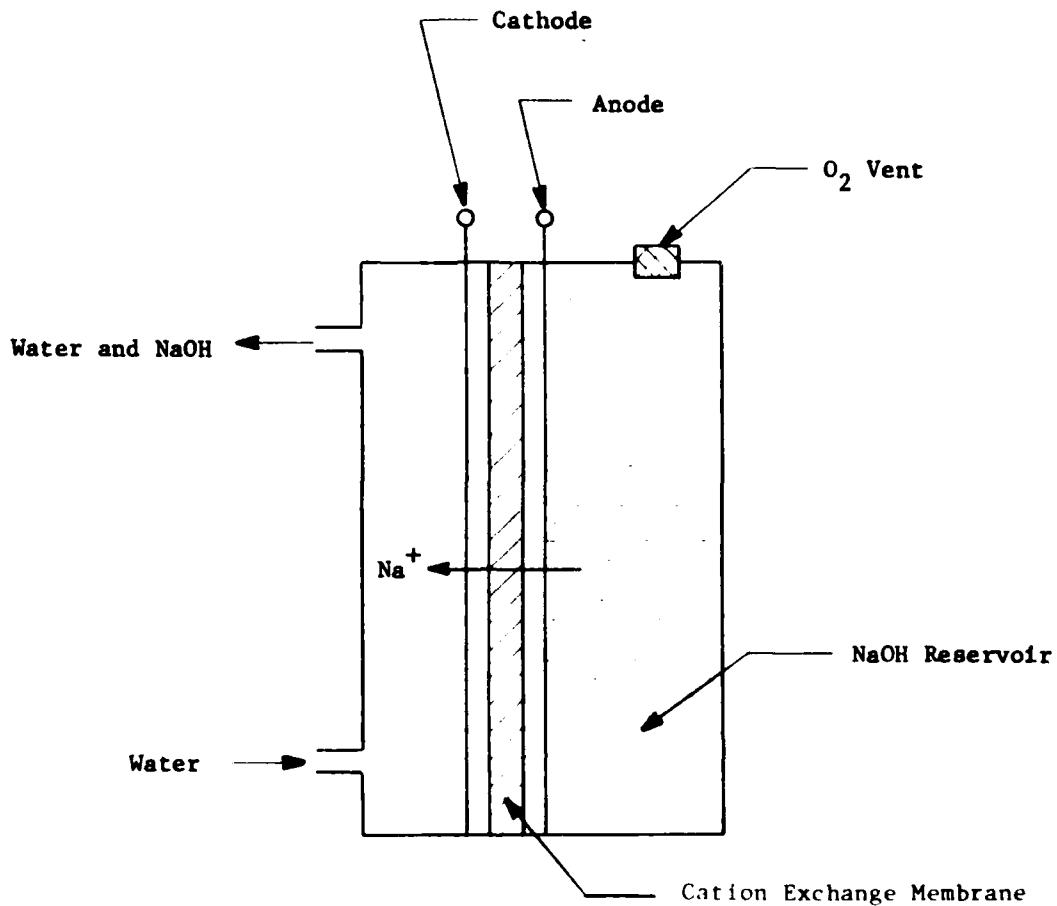


FIGURE 11 HYDROXIDE GENERATOR FUNCTIONAL SCHEMATIC

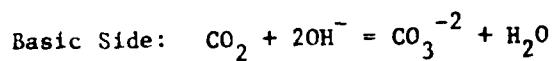
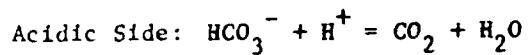
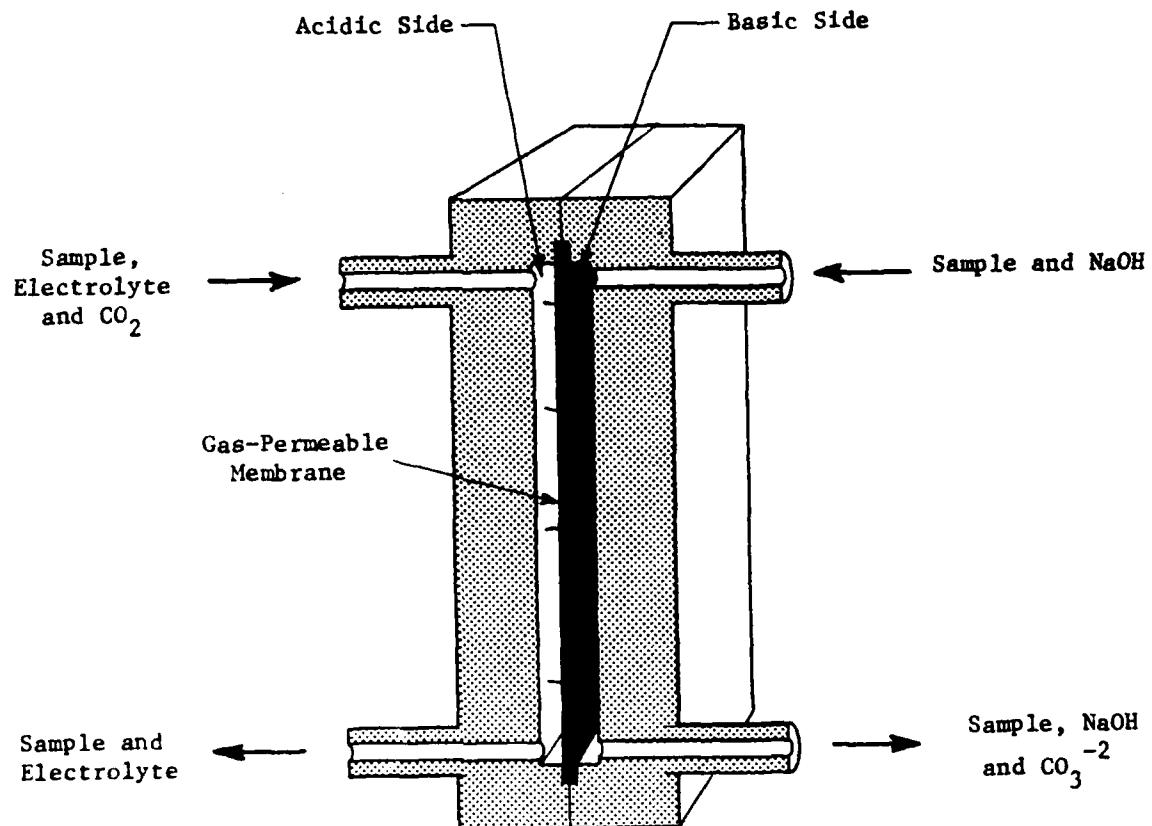


FIGURE 12 INORGANIC CARBON STRIPPER FUNCTIONAL SCHEMATIC

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Persulfate Generator. Persulfate is extremely reactive, and solutions containing persulfate are not stable for more than 24 hours. To avoid frequent replacement of the persulfate solution with fresh reagent, an electrochemical cell is included in the Advanced Breadboard Analyzer to continuously generate the persulfate required for operation. The persulfate generator is shown schematically in Figure 13. Sulfate anions (SO_4^{2-}) are electrochemically oxidized to form persulfate. Oxygen and ozone (O_3) are also generated at the anode. Hydrogen (H_2) is generated at the cathode. These gases exit through vents at the top of the anode and cathode chambers.

To maintain optimum generation efficiencies, a thermoelectric cooler is integrated into the persulfate generator to maintain the anode chamber temperature at 10 C.

The concentration of persulfate generated is controlled using a feedback control system. The persulfate generator current is increased or decreased in response to the measurement of the persulfate concentration made in the reference cell of the COD sensor, described below. In this way day to day variations in the efficiency of the persulfate generation process (due to temperature or electrolyte composition variations) can be compensated for automatically.

UV Reactor. The UV reactor consists of a housing that encloses coils of quartz and Teflon tubing (for the analytical and reference streams, respectively). The quartz coil surrounds a UV lamp which irradiates the sample/electrolyte mixture in the coil. A residence time of about eight minutes is utilized.

A blower pulls filtered ambient air through the reactor housing to cool the the reactor. This minimizes spontaneous thermal decomposition of persulfate in the reactor and maintains a high oxidation efficiency.

TOC Sensor. The membrane electrode concept was selected for use in the TOC sensor because it is responsive to CO_2 over the concentration range of the TOC Analyzer, and it is simpler and potentially more reliable than other types of CO_2 detectors.

The TOC sensor determines the concentration of CO_2 contained in the sample/electrolyte mixture by detecting the pH change caused by the diffusion of CO_2 from the sample/electrolyte mixture into an internal filling solution that contains HCO_3^- (Figure 14). The sample and internal filling solutions are separated by a gas-permeable membrane. The potential difference between the pH and reference electrodes, located in the internal filling solution, is logarithmically proportional to the CO_2 concentration in the sample solution, as shown in Figure 14. Automated electronic compensation for temperature changes is accomplished using a thermistor located in the sensor close to the pH electrode.

Steady-state sensor response is obtained when the partial pressures of CO_2 on both sides of the membrane are equal. Like all membrane electrodes, the TOC sensor requires more time for steady-state response to be achieved when the CO_2 concentration in the sample solution decreases than when it increases. This is because diffusion of CO_2 from the stagnant internal filling solution, through the membrane and into the flowing sample stream is slower than the

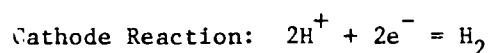
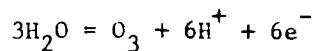
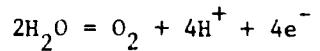
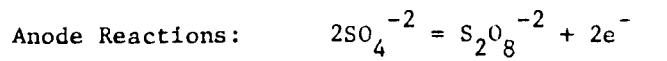
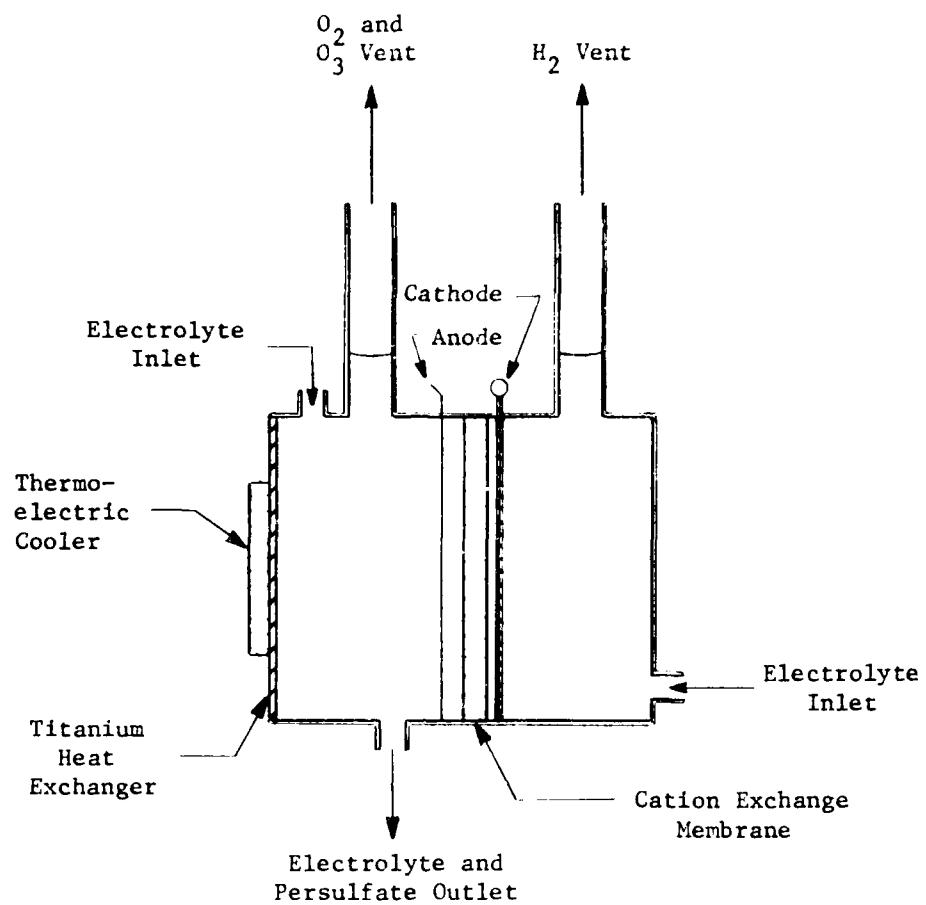
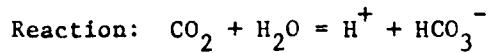
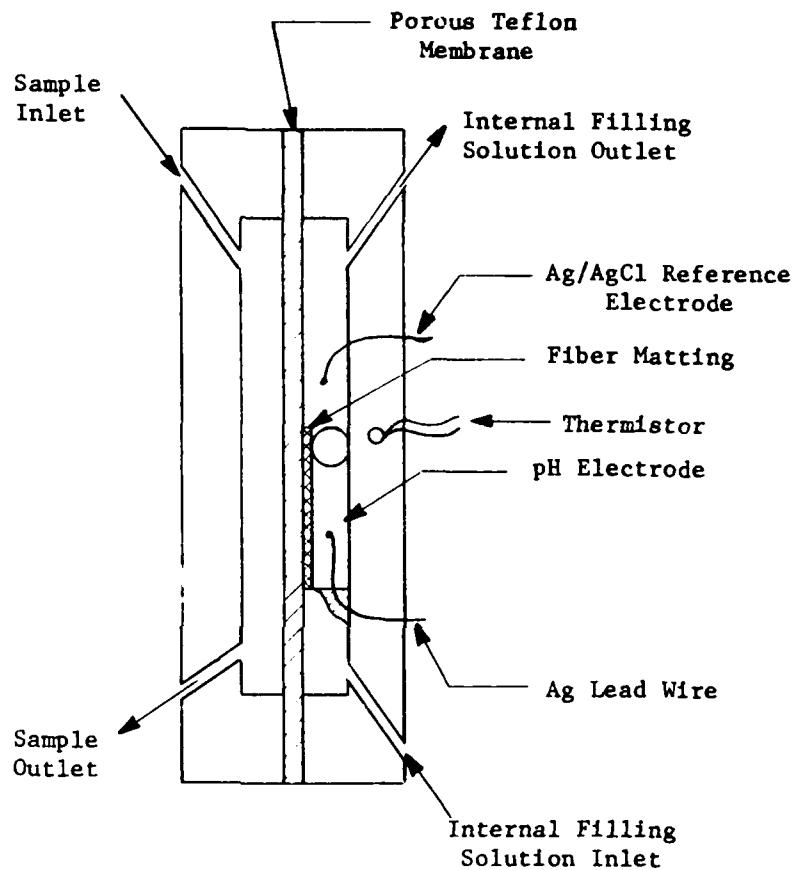


FIGURE 13 PERSULFATE GENERATOR FUNCTIONAL SCHEMATIC



$$\text{Response Equation: } E = E' + \frac{2.3RT}{F} \log (\text{CO}_2)$$

Where:

E = TOC Sensor Output, V

E' = Constant, V

R = Universal Gas Constant, 8.31 Joules/K Equivalent

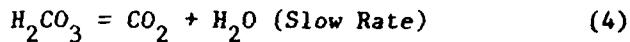
T = Temperature, K

F = Faraday's Constant, 96500 Coul./Equivalent

(CO_2) = CO_2 Concentration, M

FIGURE 14 TOC SENSOR FUNCTIONAL SCHEMATIC

reverse process. This is partly due to the difference in the rate of mass transport of CO₂ to the membrane for stagnant (internal filling solution) and flowing (sample/electrolyte mixture) solutions. Additionally, the relatively slow kinetics for the evolution of CO₂ from carbonic acid (H₂CO₃) also slows the rate of CO₂ discharge from the internal filling solution. The relative kinetics for the reactions involved in discharge of CO₂ from the internal filling solution are indicated in Equations 3 and 4:



Relying upon evolution of CO₂ from H₂CO₃, and then diffusion of CO₂ from the internal filling solution to achieve steady-state sensor response can require more than 50 minutes when the TOC concentration of the sample decreases from 100 to 1 mg/L TOC. In order to reduce this time, a fast response TOC sensor accessory was developed and incorporated into the Advanced Breadboard. This accessory consists of a solenoid pump, internal filling solution reservoir and required circuitry. It is based on the principle that the internal filling solution within the sensor is mechanically replaced with fresh solution from the reservoir every three minutes. Each TOC measurement is made immediately before the filling solution in the sensor is replaced. Therefore, after each TOC measurement, the pH electrode within the sensor is exposed to fresh internal filling solution that never has a higher CO₂ concentration than that in the sample/electrolyte mixture. Carbon dioxide always diffuses from the sample/electrolyte mixture into the internal filling solution.

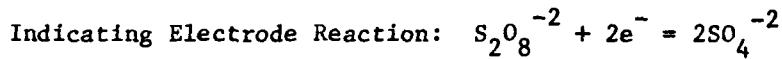
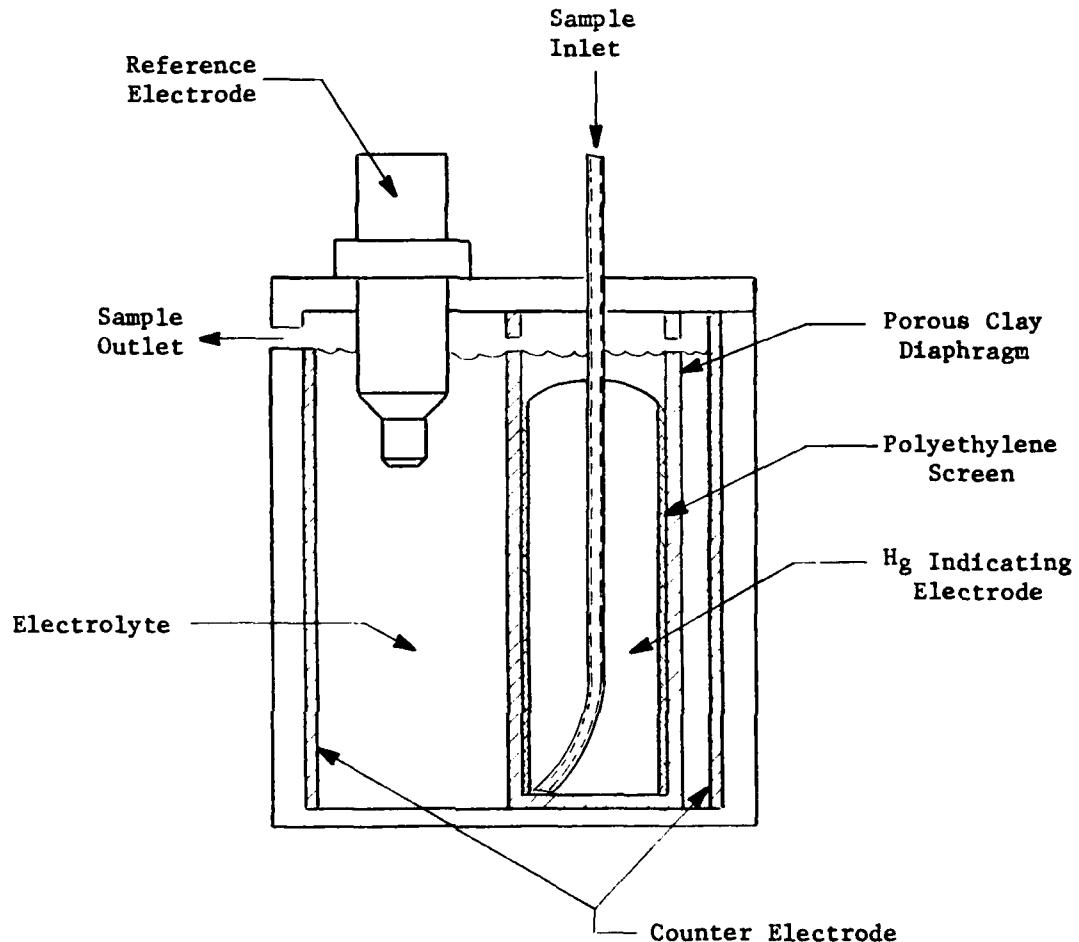
Once the internal filling solution is removed from the sensor, equilibration with air removes the excess CO₂ in the internal filling solution reservoir, and the filling solution attains its original composition.

COD Sensor. The COD sensor consists of two identical electrochemical cells (Figure 10). One of these is shown in Figure 15 with the electrochemical reactions that occur at the indicating and counter electrodes. At the indicating electrode, persulfate is reduced to form SO₄²⁻, and the resulting current is proportional to the persulfate concentration in the sample/electrolyte mixture. The COD concentration in the sample is proportional to the current difference between the analytical and reference electrochemical cells.

The indicating electrode is mercury (Hg) and is contained in a porous ceramic cup. The sample/electrolyte mixture flows between the Hg and interior surface of the porous cup. This geometry results in a high current efficiency for the persulfate reduction. By achieving this high current efficiency, the current difference between the analytical and reference cells is maximized to provide a relatively large measurement signal.

Instrumentation Package

The Instrumentation Package (Figures 10 and 11) contains the operator interfaces, process monitoring/control interfaces and the other electrical components of the Analyzer. A microcomputer in the Instrumentation Package is utilized to



$$\text{Response Equation: } I = 3.22 \times 10^{-2} G v ((\text{S}_2\text{O}_8^{-2}) + (\text{Hg}^{+2}))$$

Where:
 I = Current, A
 G = Current Efficiency, %
 v = Flow Rate, mL/min
 $(\text{S}_2\text{O}_8^{-2})$ = Persulfate Concentration, M
 (Hg^{+2}) = Mercury Concentration, M

FIGURE 15 CCD SENSOR FUNCTIONAL SCHEMATIC

perform calculations, monitor component status and control the Analyzer's operating modes. Features of the Advanced Breadboard Analyzer, made possible by the Analyzer's advanced instrumentation are listed in Table 8. Specifications of the Instrumentation Package are summarized in Table 9.

Operating Modes

The Advanced Breadboard has four operating modes: NORMAL, CALIBRATION, STANDBY and SHUTDOWN. Each of these is defined in Table 10, and allowable transitions between the modes are illustrated in Figure 16. Commands received by the Analyzer directing it to undergo other transitions are automatically rejected.

Interfaces

The Advanced Breadboard contains a full array of operator and electrical interfaces. These are described in detail below.

Operator Interfaces. Operator interfaces are located on the front panel of the Instrumentation Package. In the upper left corner of the front panel (Figure 17) the measured values are displayed. In this quadrant, a digital display is provided for carbon concentration, and indicator lights display the parameter being measured (TOC, TC or DOC). An adjustable high alarm setpoint and indicator light is provided for displaying an alarm when the carbon concentration exceeds the preset value.

At the bottom of the upper left quadrant, the COD concentration is displayed. A high alarm and setpoint indicator also are provided. Between the COD and carbon displays, a two-digit display provides for the COD/carbon ratio when both COD and any of the carbon parameters is monitored.

Analyzer controls are located on the upper right corner of the front panel. By pushing the appropriate illuminated switches, the operator can select the parameters to be measured, and can initiate operating mode transitions. Indicator lights also are located there to indicate when automatic protection (described below) of any component is off, or when automatic operation of any actuator is overridden.

Manual actuator overrides, autoprotection controls, and actuator controls are located on the recessed panel located at the bottom of the front panel. These controls are not normally required for operation, but are provided for initial Analyzer setup and debugging.

The Analyzer automatically detects failures of major components and initiates a Shutdown sequence if a failure occurs. The following components and parameters are monitored: (1) hydroxide generator voltage, (2) persulfate generator voltage, (3) persulfate concentration (determined by the reduction current in the COD sensor reference cell), (4) TOC sensor voltage, and (5) COD sensor voltage. Provisions also have been made for possible future addition of automatic protection to detect low liquid flow rates and UV lamp failure.

Controls are provided on this panel to manually control the four solenoid valves in the Analyzer, and actuator overrides are provided to activate or deactivate the hydroxide and persulfate generators, persulfate generator temperature controller, the UV reactor lamp and fan, water removal heater and fan, UV lamp, and peristaltic and solenoid pumps.

TABLE 8 ADVANCED BREADBOARD INSTRUMENTATION FEATURES

1. Automated Startup, Shutdown Procedures
2. Automated Calibration
 - Manually initiated
 - Automatically initiated every 24 hours
3. Automatic Calculation of COD/Carbon Concentration Ratio
4. Acceptance of Command Inputs for:
 - Initiation of operating mode transitions
 - Selection of measurement parameters
5. Transmittal of Status Indicators:
 - Parameters measured
 - Operating mode
 - Operating mode transition underway
6. Autoprotection
 - Rejects incorrect commands
 - Detects failure in major components -- initiates automatic shutdown
7. Fault Detection
 - Displays code identifying incorrect command
 - Displays code identifying component causing shutdown

TABLE 9 INSTRUMENTATION PACKAGE DESIGN CHARACTERISTICS

Dimensions (H x W x D), cm (in)	61x51x30 (24x20x12)
Weight, kg (lb)	32 (71)
Power Consumption, W	203
Power Source	115 VAC, 60 Hz, 2 A
Computer	
Type	SBC 80/05 (CPU 8085)
Word Size	8-Bit
Memory Size	8K
EPROM	4K
RAM ^(a)	4K
Memory Speed, Microsecond	0.9
Instruction Cycle Time, Microsecond	2.03
Input/Output	
Number of Analog Inputs	6
Number of Analog Outputs	4
Number of Digital Inputs	0
Number of Digital Outputs	16
Front Panel	
Command Inputs	5
Display Selection Inputs	5
Message Display	16
Operating Modes	
Number of Operating Modes	3
Number of Programmable, Allowed Mode Transitions	5

(a) With 96 hour battery backup.

TABLE 10 ADVANCED BREADBOARD TOC/COD ANALYZER
OPERATING MODES DEFINITION

Shutdown Mode (B)

The Analyzer is not monitoring TOC or COD. The pumps, UV reactor, cooling fan and water removal unit are off. Persulfate generator and hydroxide generator currents are zero. The TOC and COD sensors are working but their outputs are not displayed. The Shutdown Mode is called for by:

- Manual actuation
- High persulfate generator voltage
- High hydroxide generator voltage
- High COD sensor voltage
- High TOC sensor voltage
- Low TOC sensor voltage
- Low reference COD sensor current
- Unsuccessful calibration
- Mode transition from Shutdown (B) to Normal (A) or Calibration (C) was not successful

Normal Mode (A)

The Analyzer is performing its function by measuring TOC, TC, DOC, COD, TOC and COD, TC and COD, or DOC and COD, as selected by the operator. The Normal Mode is called for by:

- Manual actuation
- Completion of calibration

Calibration Mode (C)

The Analyzer is automatically performing a calibration sequence by initially zeroing its TOC and COD sensors with Standard A, then adjusting the sensors span with Standard B. Upon completion of the calibration sequence, the Analyzer reverts to the Normal Mode. The Calibration Mode is called for by:

- Manual actuation
- Automatic actuation every 24 hours

Standby Mode (D)

The Analyzer is in standby for short interruptions in normal monitoring function. No sample is introduced into the Analyzer because the peristaltic pump is off. The hydroxide and persulfate generators are off. Displays and analog outputs are disengaged. All other components are operating. The Normal Mode is called for by:

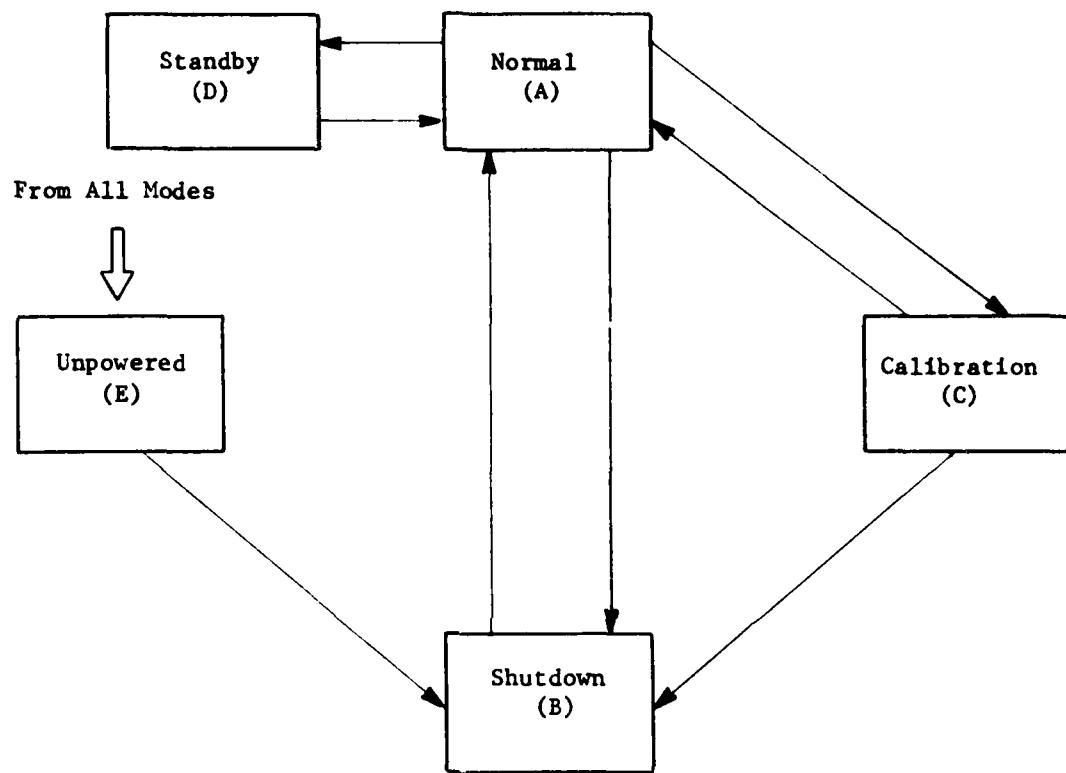
- Manual actuation

Table 10 - continued

Unpowered Mode (E)

No electrical power is applied to the Analyzer. Calibration data is stored for up to 96 hours; therefore, calibration is not required after short power failures. If the Analyzer is in the Normal Mode when a power failure occurs, the Analyzer will resume operation in the Normal Mode when power is restored. The Unpowered Mode is called for by:

- Manual actuation (disconnecting line power)
- Electrical power failure



- 5 Modes
- 4 Operating Modes
- 12 Mode Transitions
- 7 Programmable, Allowed Mode Transitions

FIGURE 16 MODES AND ALLOWABLE MODE TRANSITIONS

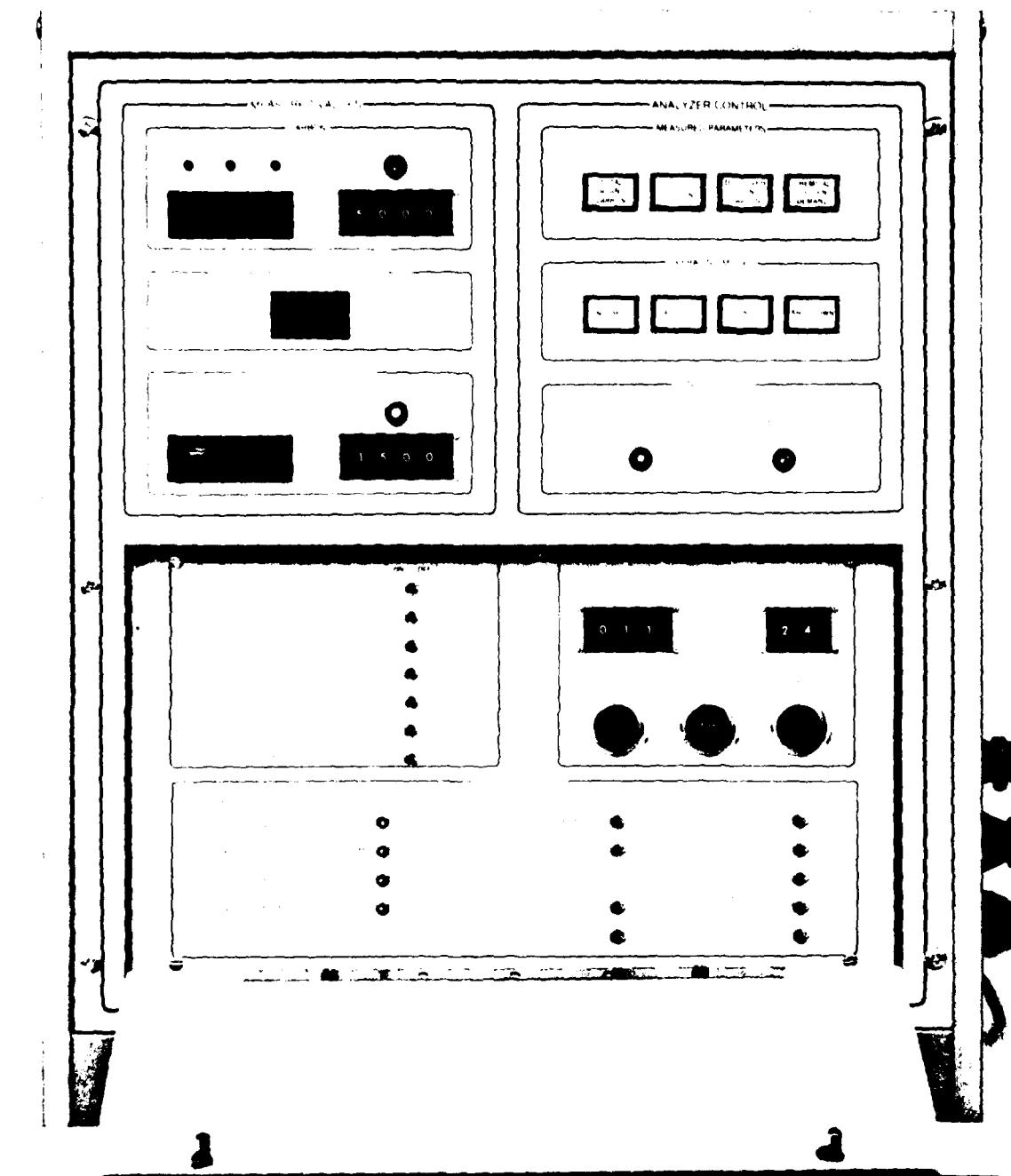


FIGURE 17 INSTRUMENTATION PACKAGE, FRONT PANEL

Actuator controls are provided to adjust critical setpoints. For example, the potential of the indicating electrodes in the COD sensor are adjustable, as are the hydroxide generator current and peristaltic pump speed.

A control is available for adjusting the COD sensor reference cell current setpoint used for feedback control of persulfate generation. The specified persulfate concentration is maintained by using the indicating current in the reference cell of the COD sensor to measure persulfate concentration. The persulfate generator current is then varied to maintain the reference cell current at the value that corresponds to the specified persulfate concentration.

The remaining control provided on this panel is the TOC correlation factor. It is an adjustment for the COD output signal and display, and applies a proportionality constant, if desired, to the measured COD values in order to achieve a 1:1 correlation between the COD values obtained with the Advanced Breadboard and COD values obtained using the standard dichromate method.

Electrical Interfaces: The electrical interfaces of the Advanced Breadboard are illustrated schematically in Figure 18. Digital inputs are provided to receive commands (0-5 VDC) from water and wastewater treatment process control monitoring instrumentation, or from remote operator control panels. These command inputs can be used to select parameters to be measured and to initiate operating mode transitions.

Analog electrical outputs (0-5 VDC) are provided for the nutrient ratio (TOC, TIC, or DOC) concentrations, COD concentration and the adjustment ratio. Overrange alarm signals (0-5 VDC) are provided for both the nutrient and off measurements.

Additional digital electrical outputs (0-5 VDC) are provided to indicate the status of the Analyzer parameter measurement and operating mode(s), and to indicate when transitions between operating modes are underway.

These electrical outputs will be valuable in most of today's wastewater treatment processes and in monitoring water quality information. With the existing interfaces, the operator of the process monitoring system or control instruments will be able to determine when problems occur and can automatically choose a sequence of shutdowns. The Analyzer's response to these events can be sequenced only when desired, and calibrated when convenient.

TEST SUPPORT ACCESSORIES

Test Support Accessories (TSA) were developed or provided by Life Systems to facilitate testing and evaluating the Advanced Breadboard.

TOC/COD Analyzer Characterization Test Stand

The TOC/COD Analyzer Test Stand was developed to support the Advanced Breadboard testing program. A major part of the test program involves introducing various synthetic and real samples into the Analyzer and recording the Analyzer's response. Correlating the composition of the sample to the Analyzer's response is the means by which the Analyzer's performance is quantified and evaluated.

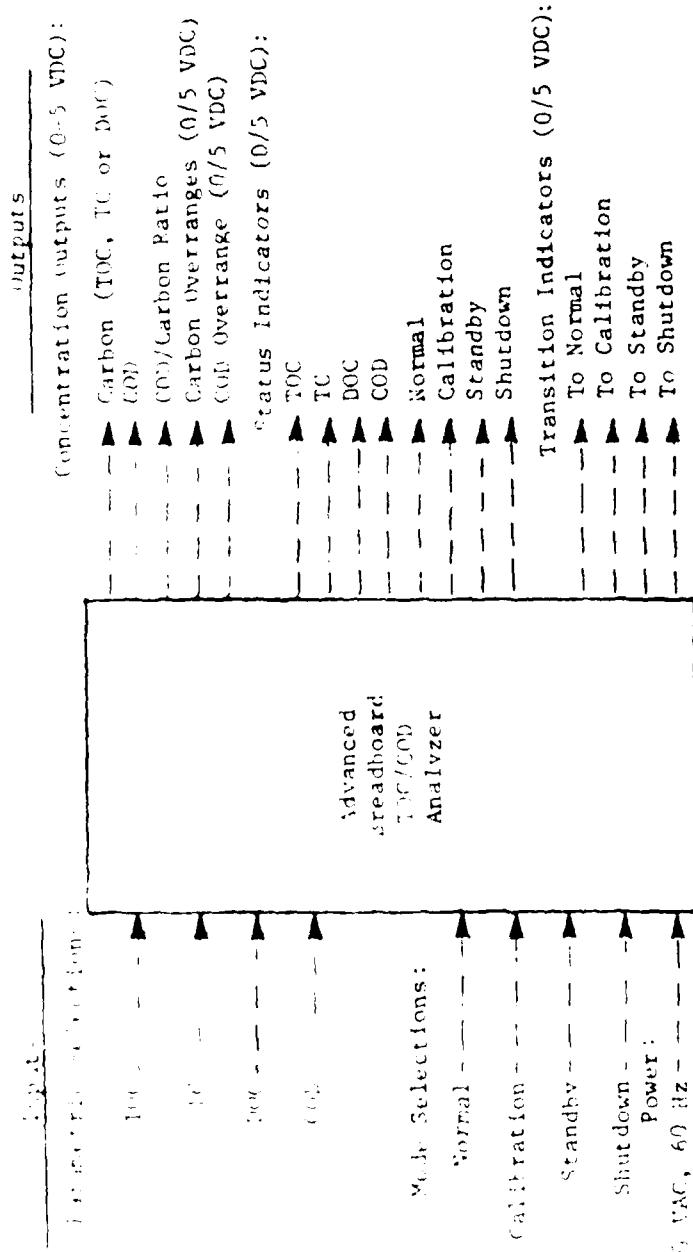


FIGURE 18 ELECTRICAL INTERFACES

The test stand (Figures 8 and 19) provides the capability for automatically sampling up to 20 samples. The sequence of samples is determined when the sample bottles are filled and the time period, during which each sample is analyzed, is selected using controls on the front of the test stand (Figure 8). Periods between 10 seconds and one hour can be chosen.

An output signal is provided by the test stand to indicate which of the samples is being analyzed. Therefore, since the composition of each sample is known, by recording this signal and the response of the Analyzer, the Analyzer's response can be correlated with the sample composition at any later time. This results in the capability for continuous, cost-effective testing of the Analyzer when the Analyzer and test stand are interfaced with an appropriate data storage and retrieval system.

A temperature controller and heat exchanger are also part of the test stand to permit quantifying the effects, if any, of sample temperature variations on the performance of the Analyzer. Temperatures within the range of 0 to 40 C (32 to 104 F) can be used.

Data Acquisition and Reduction System

A Data Acquisition and Reduction System (DARS) was developed under Life Systems' IRAD program and made available for automated data storage and retrieval during this test program. The DARS is shown in Figure 20 with a line printer provided for retrieval of hard copies of test data.

The DARS is capable of recording data using up to 32 analog (0 - 5 VDC) sensor inputs and up to 16 digital (0/5 VCD) inputs. The period between data sampling and storage can be adjusted from between 1 second to 18 hours.

The DARS provides the data storage and retrieval capability necessary to record the Analyzer's response to each sample and the signal from the test stand that identifies that sample. Operating the DARS with the test stand permits unattended testing of the Analyzer and, later, cost-effective retrieval and reduction of data.

TEST PROGRAM

The Advanced Breadboard test program has been started and is scheduled to be completed after the period covered in this report. Future documents will present the results of the total test program.

The goals of this testing are to (1) check out the Advanced Breadboard Analyzer, to detect problem areas, identify corrective actions, and implement those actions when practical, (2) to test the dynamic interactions between Analyzer components that may affect overall Analyzer performance, and which, prior to development of the Advanced Breadboard, could not be tested, (3) verify that the analytical performance of the Advanced Breadboard is comparable with that projected by prior tests of the Laboratory Breadboard, and (4) to evaluate the accessories, features and capabilities incorporated for the first time into the Advanced Breadboard in order to determine the magnitude of the benefits they provide and to detect any problems that might exist.

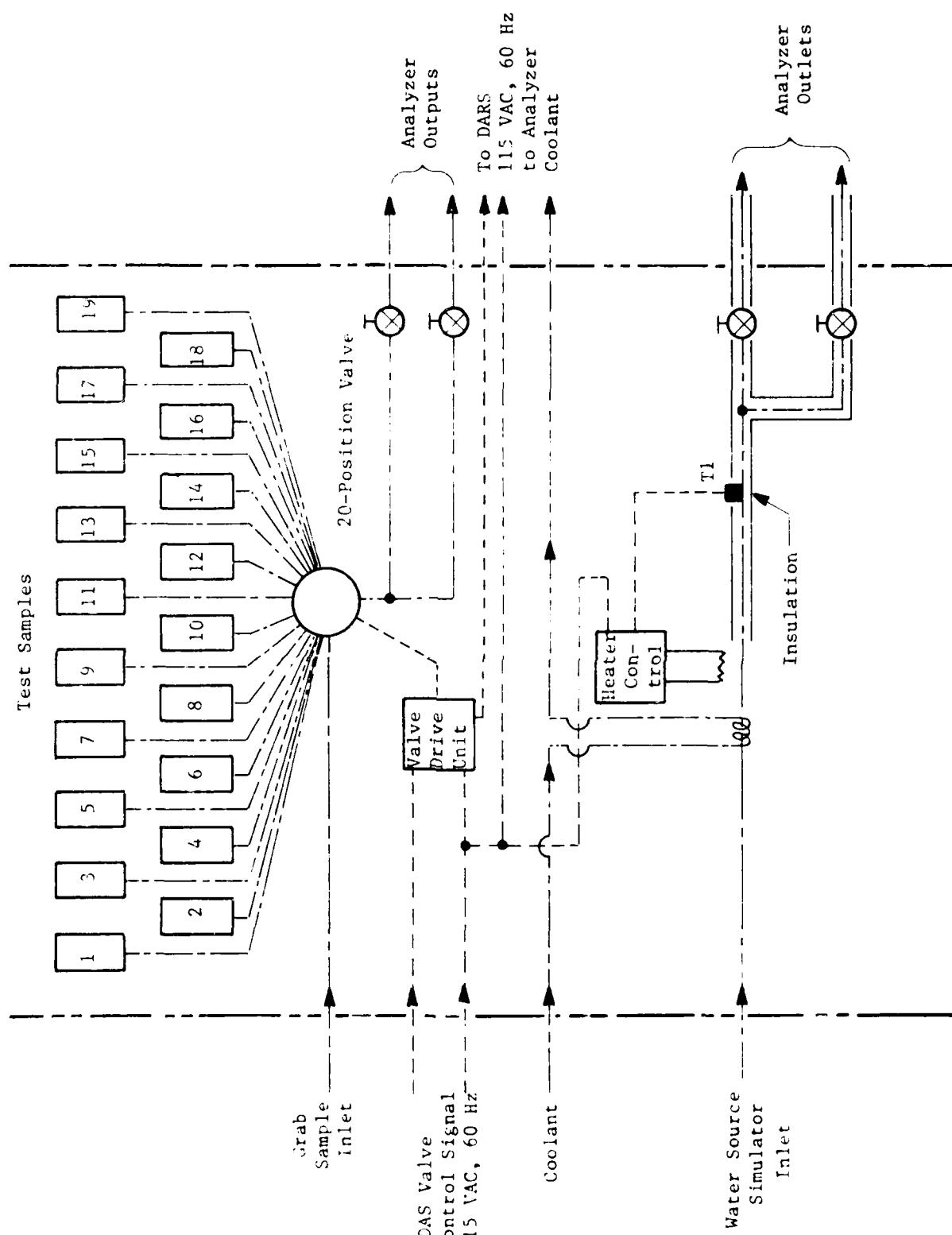


FIGURE 19 TOC/COD ANALYZER CHARACTERIZATION TEST STAND

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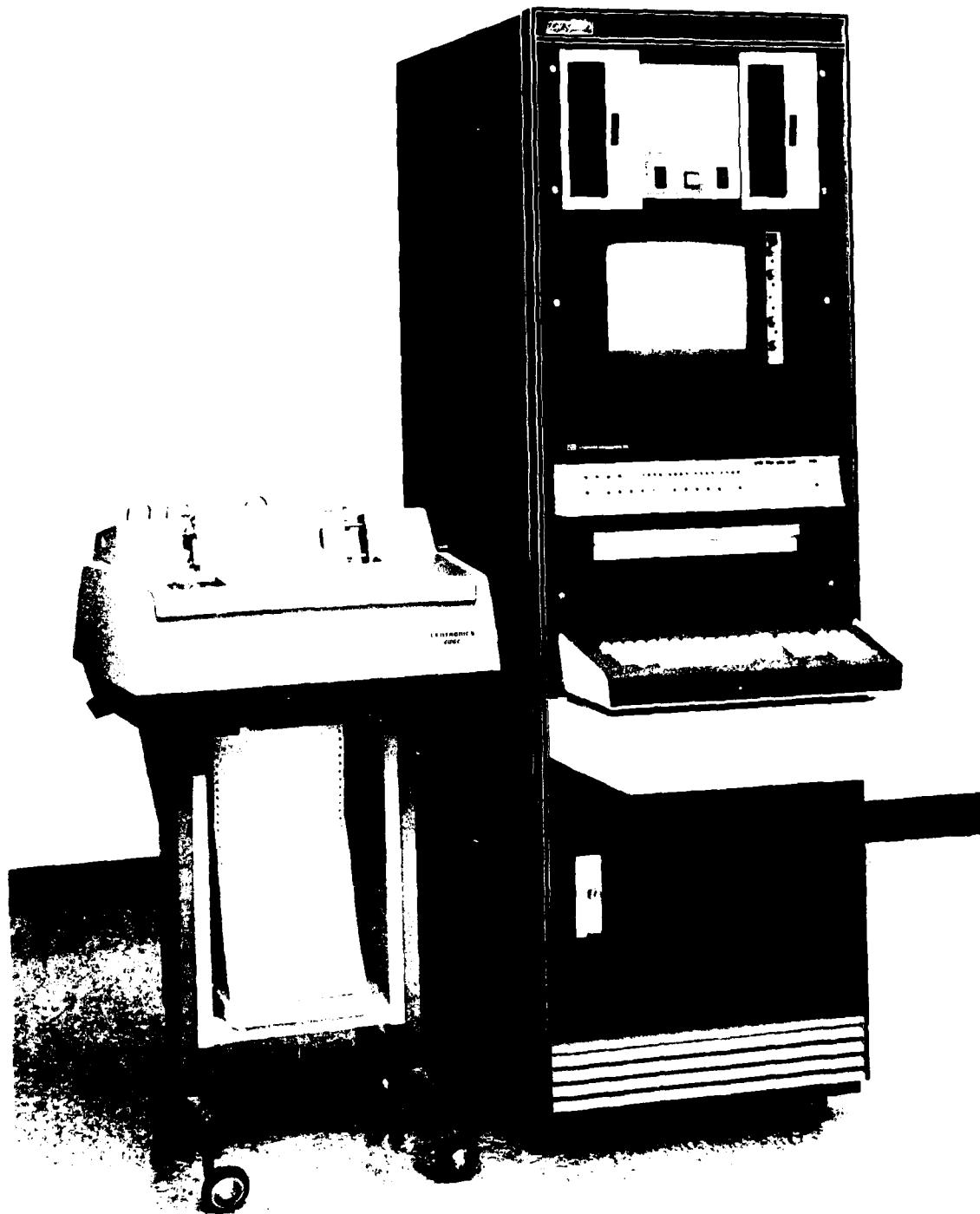


FIGURE 20 DATA ACQUISITION AND REDUCTION SYSTEM

At the time of this report, the Analyzer Checkout Tests have been completed and the Design Verification Test has been started.

Checkout Tests

Checkout Tests were performed on the pumps, TOC and COD sensors, UV reactor, inorganic carbon stripper, autocalibration accessory and other major components and accessories. Significant results of the Checkout Tests are described below.

Hydroxide Generator Checkout

The hydroxide generator was designed to inject 0.05 M NaOH into the sample stream with a current of 26 mA (Figure 21). This data was projected on the basis of tests of an electrochemical cell similar to the hydroxide generator, but which contained a solution of 0.1 M potassium hydroxide (KOH) in the accumulator.

The hydroxide generator in the Advanced Breadboard operates with the accumulator filled with NaOH pellets and water. As is apparent in Figure 21, the larger concentration of base in the accumulator establishes a greater driving force for diffusion of base through the cation exchange membrane, resulting in a significant concentration of NaOH in the sample stream even in the absence of current.

A method of controlling the rate of NaOH diffusion was investigated. Half of the cation exchange membrane was masked with a Teflon film to prevent diffusion of NaOH through that half of the membrane. The center curve in Figure 21 is the data obtained with the generator masked in this way. These data show that the rate of diffusion can be controlled by reducing the membrane area in the hydroxide generator.

The data in Figure 21 also suggests the future versions of the Analyzer may be simplified by using the diffusion process alone, without the necessity of supplying current to generate the NaOH. This would eliminate the need for the power supplies, actuator driver and control circuitry in the Analyzer, and would have a significant cost reduction benefit.

Inorganic Carbon Stripper Checkout

The checkout of the inorganic carbon stripper consisted of a determination of its IC removal efficiency. Solutions containing known concentrations of sodium bicarbonate (NaHCO_3) were pumped through the stripper. The IC remaining in the stripper effluent was measured using the TOC sensor, which had been calibrated with standard NaHCO_3 solutions immediately prior to the test.

Figure 22 shows the results of this test. For concentrations up to 250 mg/L IC, the efficiency of IC removal was approximately 98% and at the 100 mg/L IC concentration (the highest concentration for which the stripper was designed) the residual IC concentration was only 1.5 mg/L.

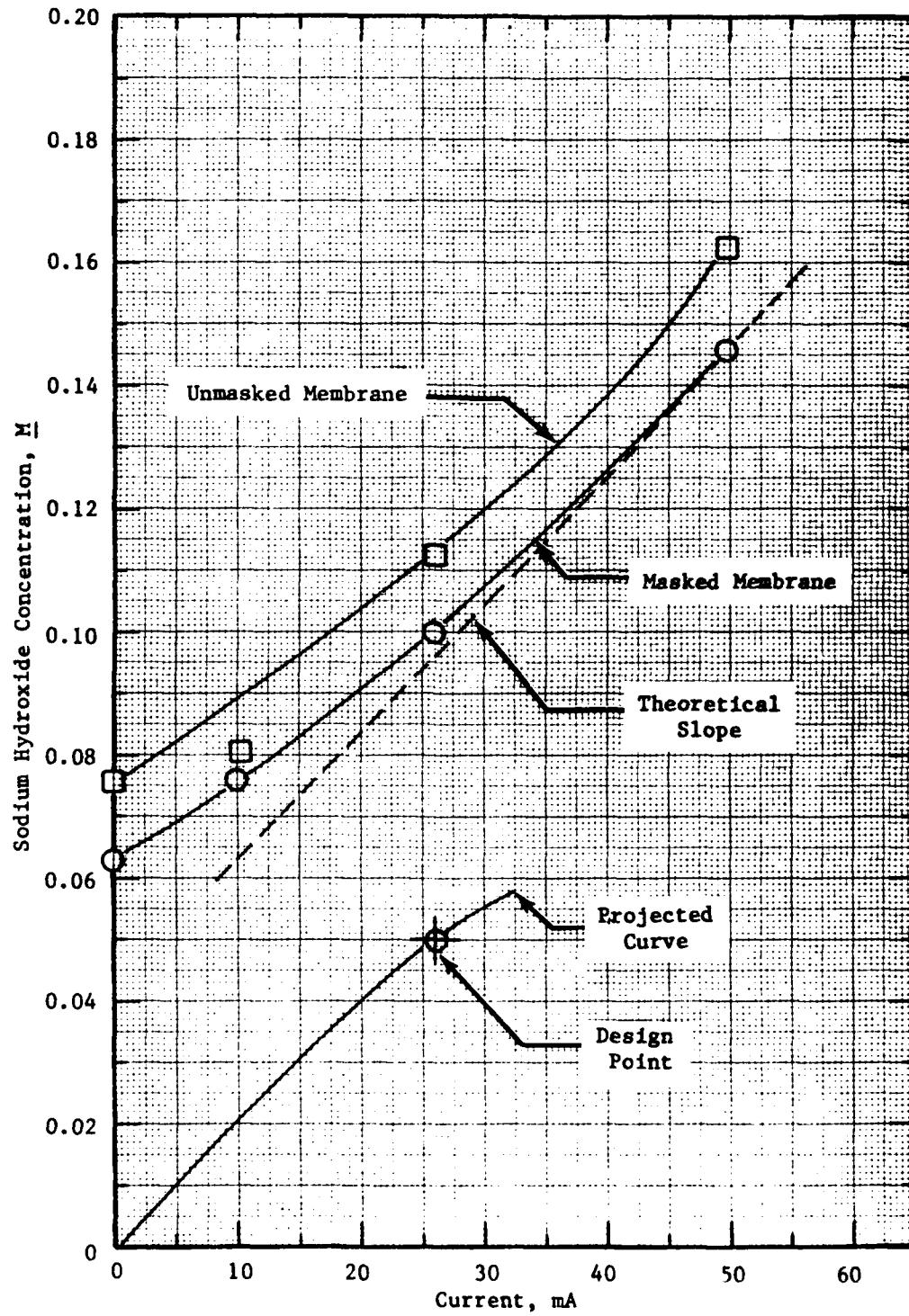


FIGURE 21 HYDROXIDE GENERATOR CALIBRATION CURVES

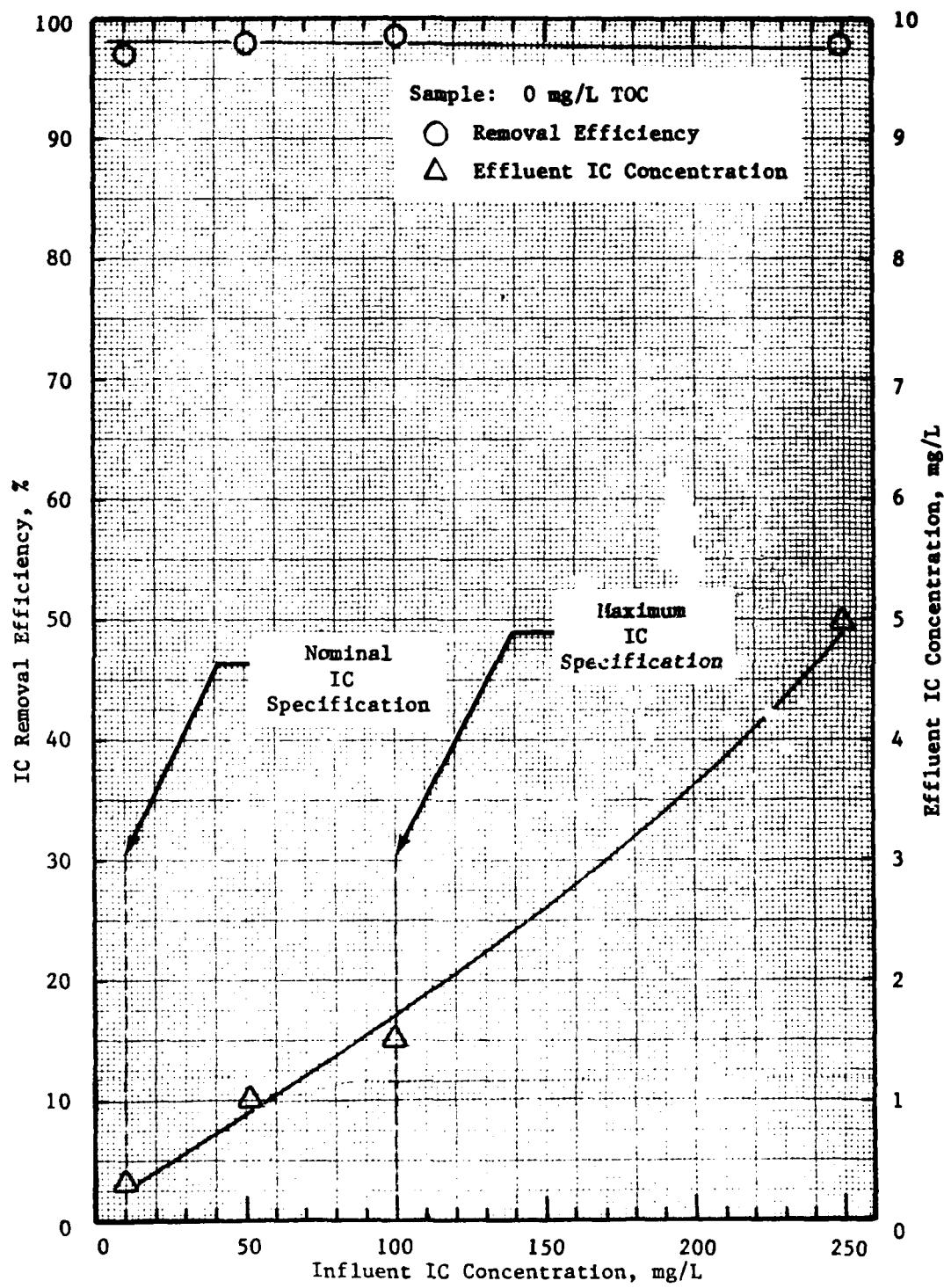


FIGURE 22 INORGANIC CARBON STRIPPER EFFICIENCY

This test has therefore demonstrated that the stripper is an effective method of removing IC from the sample. Total organic carbon and DOC measurements can be expected not to be in error by more than 1.5 mg/L, due to residual IC. For the majority of samples in which the IC concentration is less than 50 mg/L, any error due to residual IC will be less than 1 mg/l.

Persulfate Generator Checkout

The Advanced Breadboard Analyzer's persulfate generator was scaled up from the laboratory breadboard generator tested in the Key Components Evaluation.⁽²⁾ The generator tested here was designed to produce 0.27 M persulfate at a current of 330 mA (Figure 23). Its actual performance agrees closely with the projected performance. The required concentration is achieved at a current of 440 mA, well within the maximum current of 500 mA which can be provided to the cell.

The Checkout Test and subsequent operation of the persulfate generator have demonstrated that electrochemical generation is a practical and effective method of producing persulfate solutions on a continuous basis, and minimizes the need for periodic manual reagent preparation.

UV Reactor Checkout

The UV reactor Checkout Test was performed primarily to demonstrate the mechanical and electrical integrity of the reactor, rather than to quantify the oxidation efficiency. The UV reactor was demonstrated to operate effectively, and no mechanical or electrical problems were encountered.

In preparation for later tests of the Analyzer's response to selected organic solutes, a test of the reactor's oxidation efficiency was performed using samples containing KHP. The oxidation efficiency was determined using the TOC sensor, calibrated with NaHCO₃ solutions, to measure the CO₂ produced in the KHP oxidation.

The results of this preliminary test (Figure 24) indicate that the KHP is completely oxidized at the design specification of 100 mg/L TOC. However, at the design goal of 500 mg/L, incomplete oxidation was achieved. Precise data is not available because of reasons described below, related to the TOC sensor performance. However, the effluent of the UV reactor was somewhat discolored, indicating that oxidation of the organic material was incomplete. This data suggests that a future activity will include an investigation and optimization of the organic oxidation process.

TOC Sensor Checkout

The TOC sensor was assembled and checked out by measuring its response to standard solutions containing NaHCO₃. The response curve of the sensor is shown in Figure 25, and agrees well with the curves obtained for other available sensors.⁽²⁾ The response of the sensor was a logarithmic function of concentration between 5 and 500 mg/C C. Below 5 mg/L, some nonlinearity was observed. On the basis of these results, it was concluded that the TOC sensor operated as anticipated, and it would provide a reliable method of measuring CO₂ in the Analyzer.

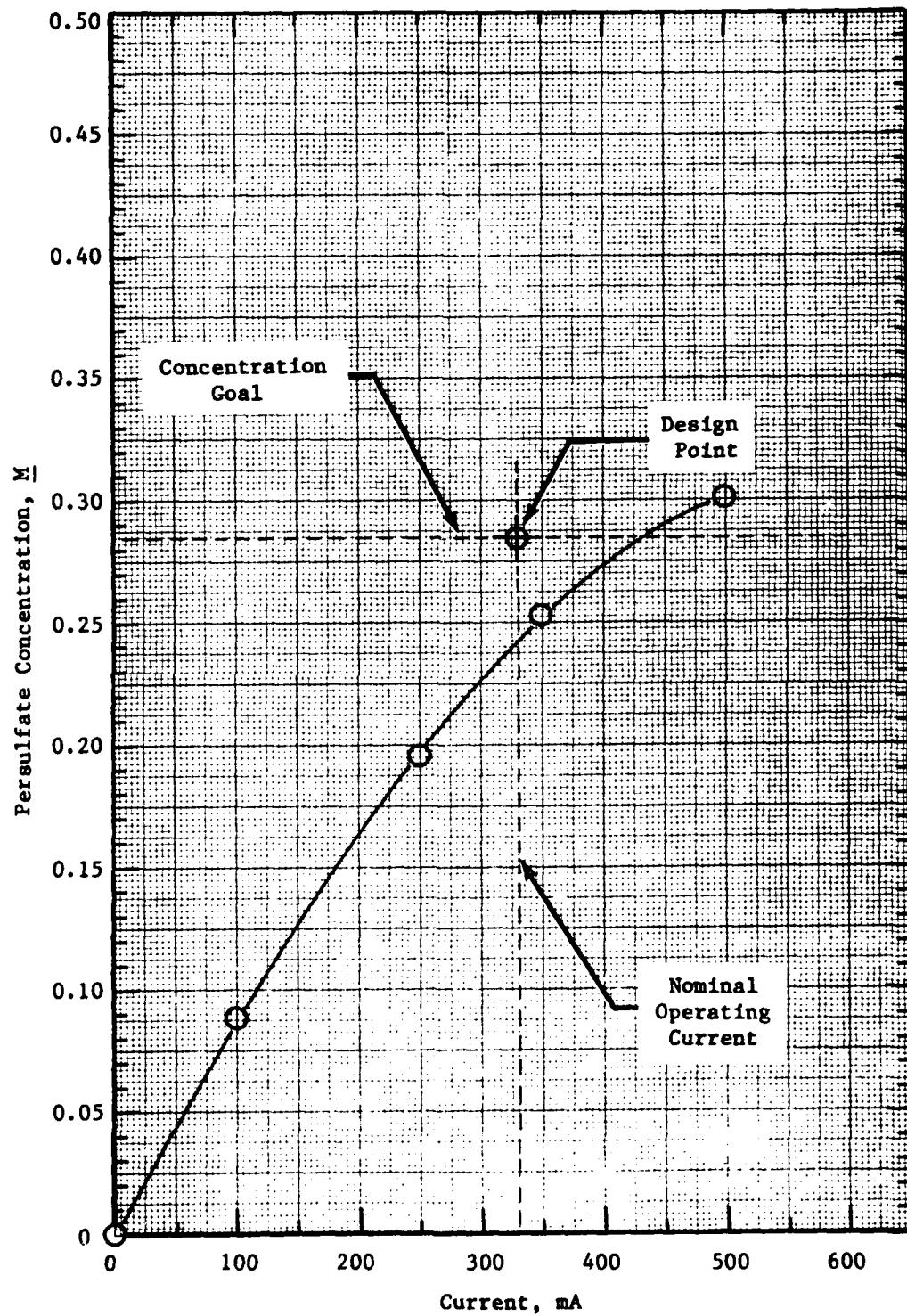


FIGURE 23 PERSULFATE GENERATOR PERFORMANCE

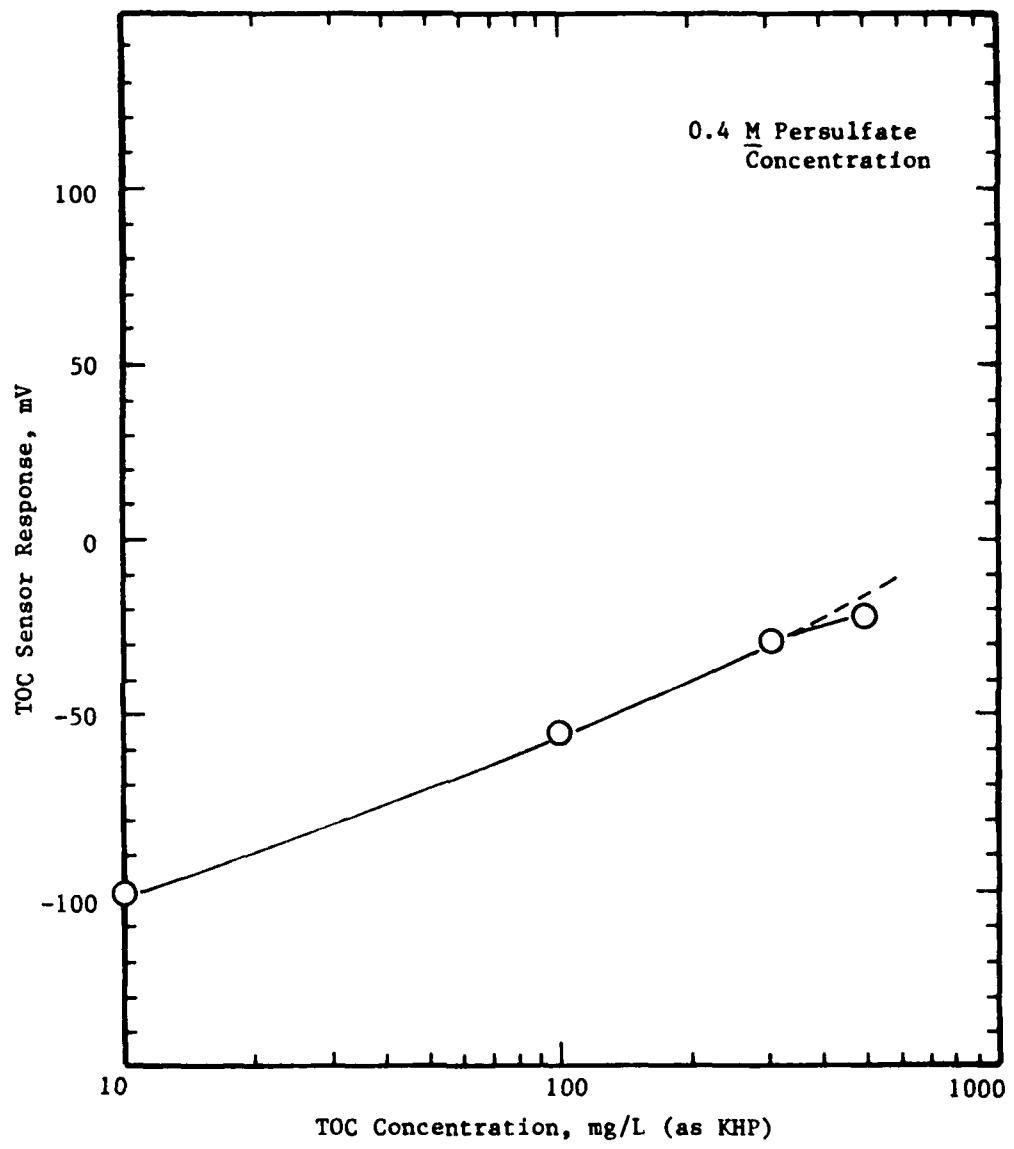


FIGURE 24 RESULTS OF UV REACTOR CHECKOUT TEST

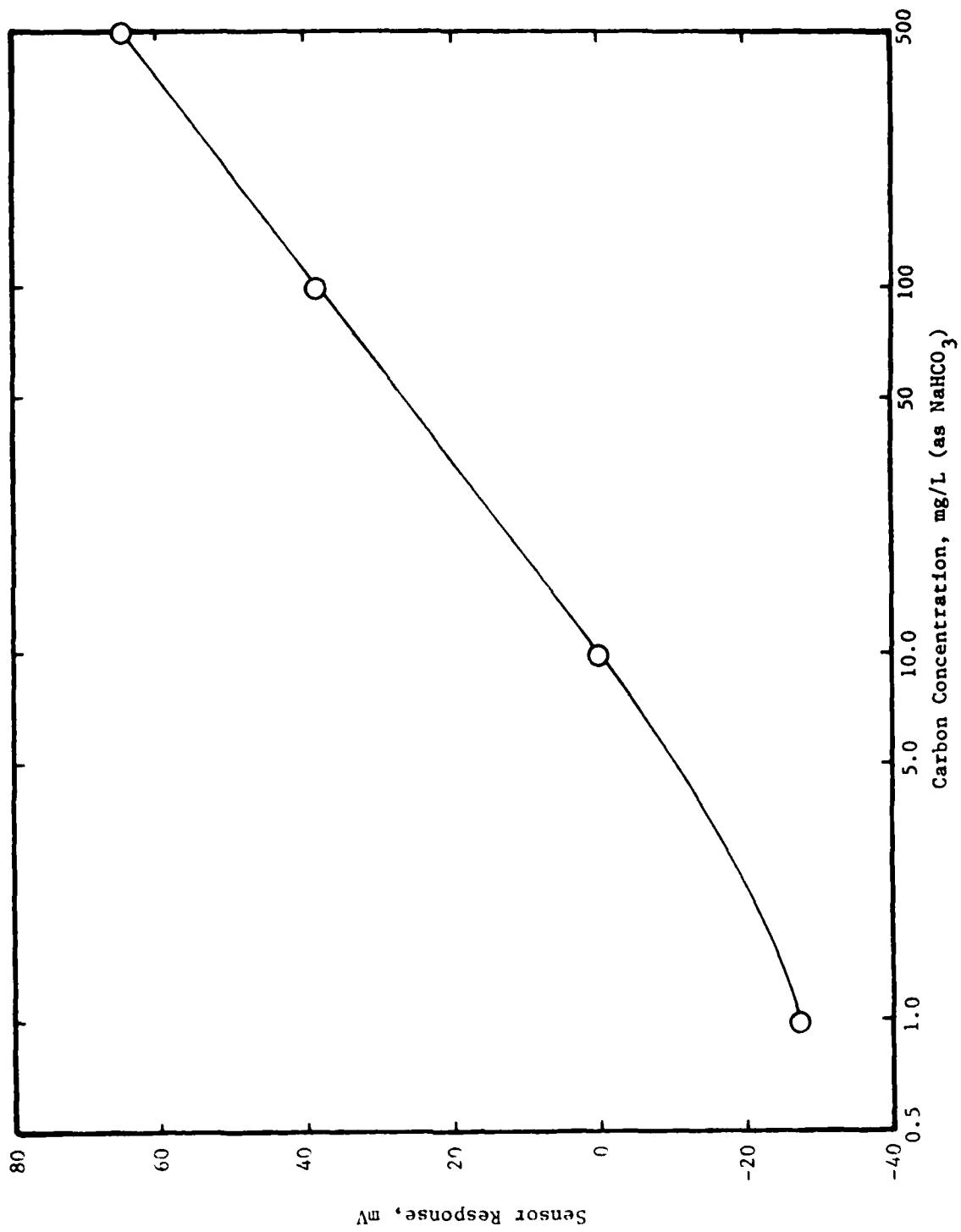


FIGURE 25 RESULTS OF TEC SENSOR CHECKOUT TEST

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In later testing, however, it was found that the TOC sensor performance changed during operation. First, the absolute value of the sensor potential for a given TOC concentration changed from day to day. Second, the sensor became less logarithmic in its response characteristics. These changes can be seen by comparing the sensor response curve shown in Figure 26 to that obtained about two months earlier (Figure 25).

Investigations into the causes of these changes resulted in the following conclusions:

1. The miniature pH electrode in the TOC sensor, used to achieve a compact sensor configuration, is potted into the sensor housing. This arrangement provides an insufficient barrier to prevent moisture from the internal filling solution from reaching the silver wire that emerges from the pH electrode. Because of the extremely high impedance of the pH glass, even a trace of moisture in contact with the wire will significantly alter the electrode potential. Since the amount of liquid contact varied daily, the potential varied from day to day.
2. Trace contaminants in the filling solution are present which eventually coat the pH sensor, altering the shape of its response curve, and altering the potential of the silver/silver chloride (Ag/AgCl) reference electrode in the sensor. The geometry of the TOC sensor does not lend itself to easy cleaning of the pH electrode. Because the electrode is potted into the housing, removal of the electrode for cleaning is impossible.

To eliminate these problems, it was decided to alter the sensor to accommodate using a commercially available combination pH/reference electrode. The sensor will be modified so that it can be removed for cleaning, or replaced if necessary. The reference electrode will be enclosed in the electrode, electrically connected to the internal filling solution only through a salt bridge. Therefore, impurities in the filling solution will not affect its potential. Also, moisture will not be able to contact the wiring. Therefore, this modification is expected to effectively prevent the response changes observed in the present sensor.

This sensor modification is presently underway and will be reported in greater detail in the future.

COD Sensor Checkout

The COD sensor Checkout was performed to verify the mechanical, electrical and electrochemical integrity of the sensor and to operate a differential persulfate sensor for the first time. The checkout demonstrated that mechanical, electrical and, apparently, the electrochemical aspects of the sensor operated as anticipated. However, the differential response of the sensor was found to fluctuate because of liquid flow rate differences between the analytical and reference cells. The current measured in each cell is flow-dependent, and is proportional to the linear flow rate of liquid entering the cell. As bubbles are generated in the UV reactor (from the formation of CO₂ from organic oxidation, or O₂ from decomposition of water by persulfate) the linear flow rate of the stream

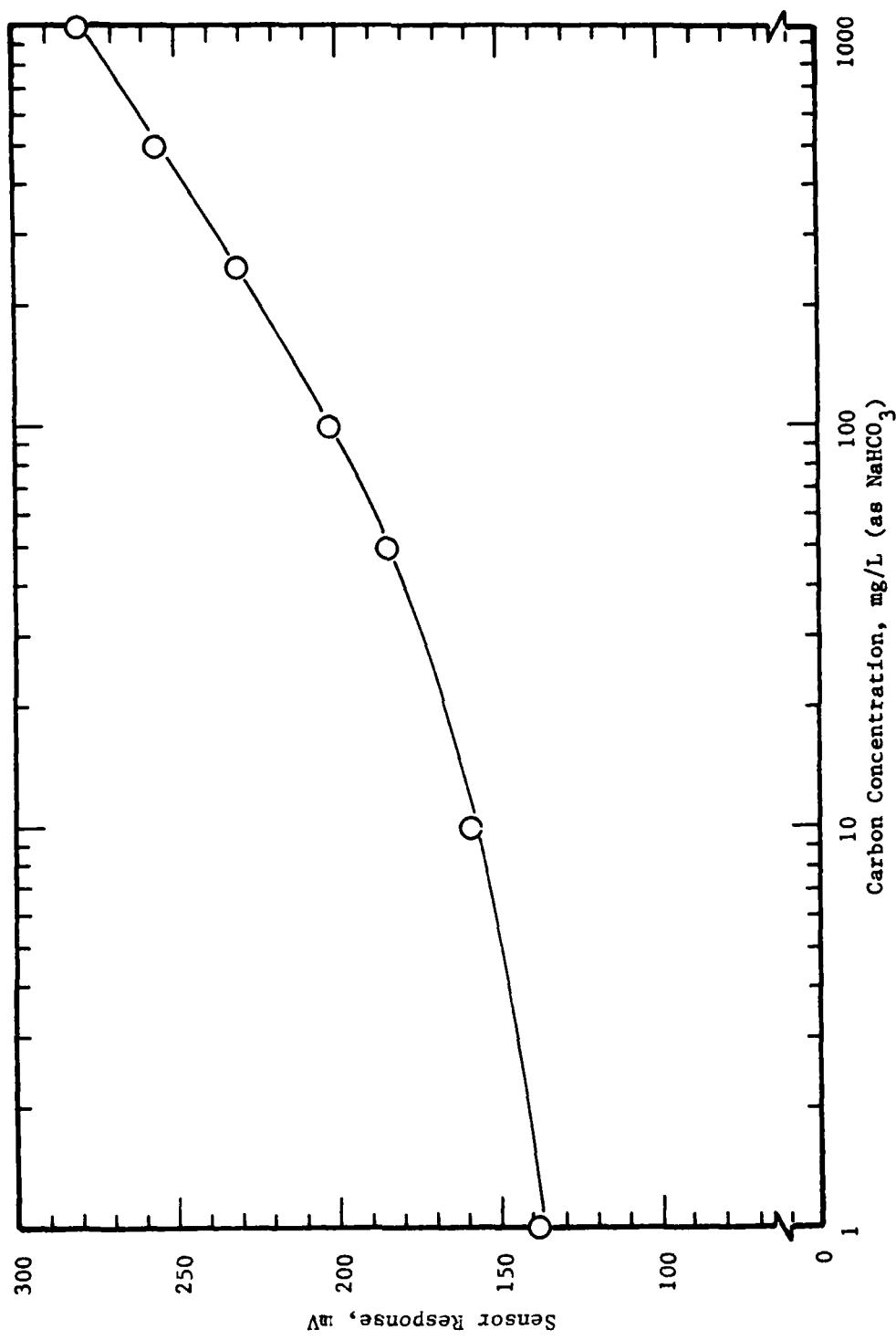


FIGURE 26 TOC SENSOR RESPONSE AFTER TWO MONTHS

entering the analytical cell becomes greater than that of the reference cell. Since bubble formation is unpredictable, the current difference between the two cells in the sensor varies in an unpredictable way. This problem may be solved by incorporating a bubble elimination device between the UV reactor and the COD sensor.

The COD sensor is also vibration sensitive. This results from surface area changes in the Hg indicating electrodes when they are vibrated. Currents due to the changing electrode surface area occur because of capacitive effects and electron-transfer reactions between the solution and the electrode.

A possible solution of this problem is to enclose the indicating electrodes such that vibrations cannot cause electrode surface area changes.

Beyond these phenomena, other causes of the sensor response fluctuations might exist. Sufficient time has not been available to completely characterize the sensor's performance, and further work on the COD measurement function is planned after the TOC measurement function is fully operational and evaluated.

Shakedown Test

During the Shakedown Test the Advanced Breadboard was operated for eight hours. During this period the operating mode transition sequences were tested. The Analyzer successfully underwent transitions from the Unpowered Mode to Shutdown; Shutdown to Normal; Normal to Calibration and back to Normal; and, at the end of the test, Normal to Shutdown.

No component failures or unanticipated system shutdowns were experienced.

Design Verification Test

The Design Verification Test (DVT) consists of tests of the Analyzer's response to selected organic solutes and potential interferences, and a determination of the precision and day-to-day reproducibility of the Analyzer's response. At this time the DVT is underway, but not completed.

The IC interference test has been completed. Data, using the TOC sensor in its original form, obtained is shown in Figure 27. The Analyzer was calibrated for this test using the automated calibration sequence with 3 and 300 mg/L TOC (as KHP) calibration standards. Then samples containing 10 mg/L TOC (as KHP) plus various concentrations of NaHCO₃ were analyzed. Since TOC was measured, the IC in the sample was removed by the inorganic carbon stripper.

As expected on the basis of the inorganic carbon stripper Checkout Test, the presence in the sample of as much as 100 mg/L IC increased the measured TOC concentration by less than 1 mg/L. However, the Analyzer reported a concentration of 6 mg/L TOC, rather than the expected 10 mg/L, because of the non-linear response characteristics of the sensor, discussed above. The inaccuracy produced by the nonlinear sensor response is anticipated to be eliminated by the TOC sensor modification now underway.

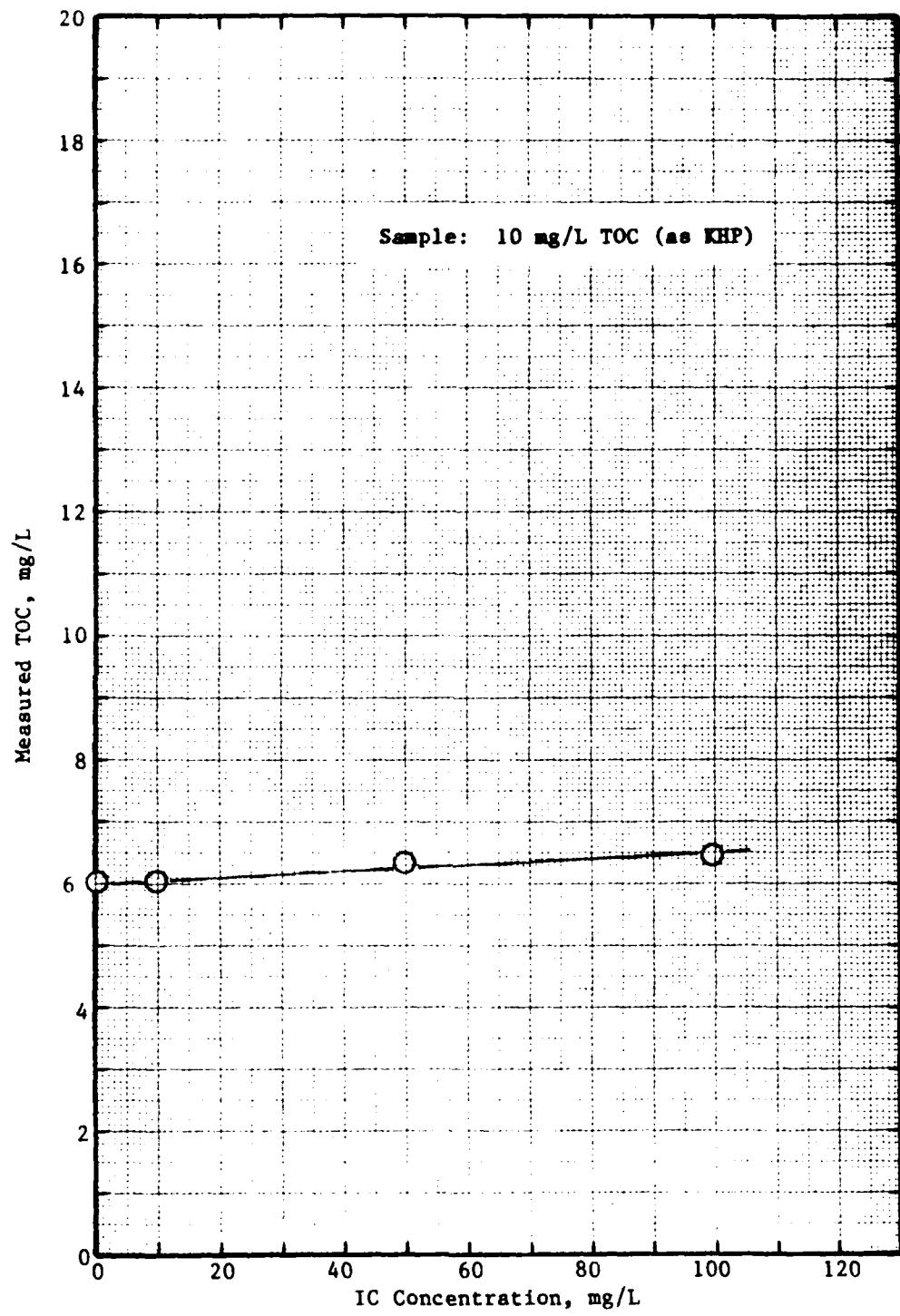


FIGURE 27 RESULTS OF IC INTERFERENCE TEST

CONCLUSIONS

The Advanced Breadboard TOC/COD Analyzer has been designed, fabricated, assembled and checked out. Activities are underway for the completion of the test program for the TOC portion of the Analyzer. Efforts are also scheduled for incorporating a method of eliminating measurement errors due to Cl⁻ in samples. Once these activities are completed, it is recommended that development of the COD portion of the Analyzer be completed.

The Advanced Breadboard has already incorporated/demonstrated several unique features that will provide valuable information, or would permit more effective utilization of the Analyzer in process monitoring/control applications and water quality monitoring in remote locations. These features are:

1. Automated, continuous operation.
2. Measurement of TOC, TC, DOC, COD or simultaneous measurement of COD and any of the other three parameters.
3. Automatic calculation and display of COD/carbon ratios.
4. Automatic, operator-initiated Startup, Calibration and Shutdown sequences.
5. Autocalibration (automatic zero and span adjustments) automatically initiated every 24 hours.
6. In situ generation of NaOH and persulfate reagents.
7. Electrolyte recycle loop for extended operation without manual electrolyte replenishment.
8. Autoprotection and fault isolation logic.
9. Electrical command inputs for integration of the Analyzer in automated process instrumentation, and for operation using remote operator controls.
10. Electrical outputs for use in process monitoring/control, and transmittal of data and Analyzer status:
 - a. Carbon concentration
 - b. COD concentration
 - c. COD/carbon ratio
 - d. Concentration overrange indicator (carbon and COD)
 - e. Monitored parameter indicator (TOC, TC, DOC and COD)
 - f. Operating mode indicator (Normal, Calibration, Standby and Shutdown)
 - g. Operating mode transition indicator

There are components and features that remain to be demonstrated in the future. These include the modified TOC sensor, upgraded to incorporate a combination pH/reference electrode. This revised sensor is being modified to increase the reproducibility of TOC measurements and to permit simplified cleaning of the pH sensor when required.

For the first time it has been possible to schedule the development of a method for eliminating organic concentration measurement errors caused by Cl⁻ in the water samples. During the upcoming year, candidate methods will be evaluated, an optimum method will be identified and it will be incorporated into the Advanced Breadboard for testing and evaluation with synthetic and environmental samples.

Upon completion of these activities, the only major activity remaining that involves the Advanced Breadboard is the characterization of the COD sensor and identification of any changes that may be required to integrate the sensor into the Analyzer. With the upgraded sensor, the analytical performance of the COD measurement will be demonstrated and evaluated in the same way that the TOC measurement is now being evaluated.

The Advanced Breadboard was developed to be a test bed for cost-effective demonstration of new analyzer features and components. It was designed to provide flexibility in component configuration, and the operating parameters of the components. In all of this, the Advanced Breadboard development has been more than successful. Future testing and development activities will be performed efficiently and in a timely manner as the result of the Analyzer development just completed.

RECOMMENDATIONS

It is recommended that activities covering the scheduled testing and evaluation of the TOC portion of the Advanced Breadboard, and the development and incorporation of the method for eliminating Cl⁻ effects be completed as planned.

Upon completion of these activities, it is recommended that efforts be undertaken to complete development of the COD portion of the Analyzer. This activity will be limited to work on the COD sensor, since all other Analyzer components will have been thoroughly tested during the development of the TOC portion. An intensive characterization of the COD sensor will be performed to identify any parameters, aside from the already noted effects of vibration and flow variations, that impact sensor performance. Changes required to eliminate these effects will be defined and implemented. Then the modified sensor will be integrated into the Advanced Breadboard Analyzer and the analytical performance of the COD measurement will be tested and evaluated.

This approach is recommended primarily because of the benefits it provides in terms of concentrating program resources to effectively address and solve the few remaining technological problems in the development of the TOC/COD Analyzer. By approaching these efforts in a sequential fashion, the development of the Advanced Breadboard Analyzer can be completed. Future efforts can address the development of instrumentation to be used in field tests and extended on-site evaluations of the TOC/COD Analyzer for the future applications planned for it.

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